Photochemical Assessment Monitoring Stations (PAMS) Performance Evaluation Program

Final Report

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DISCLAIMER

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ABSTRACT

Humidified performance evaluation samples containing volatile organic compounds were prepared for PAMS in 6-liter SUMMA®-polished stainless steel canisters. Before preparation, each canister was cleaned and certified for total nonmethane organic compound (NMOC) content to less than 10 ppbC, and analyzed by gas chromatograph/mass spectrometer-flame ionization detector (GC/MS-FID) to verify cleanliness on a compound-specific basis. Performance evaluation samples were prepared from high pressure multiple-component gas cylinders obtained from a specialty gas manufacturer at a pressure of approximately 30 psig with a relative humidity of about 70%. The canisters were prepared at a concentration appropriate for direct analysis by the analytical system without the use of any slip-stream or pressure reduction devices. Each canister was analyzed by Eastern Research Group (ERG) prior to shipment to the PAMS participants, and the results of the ERG analyses were pooled to provide a range of two standard deviations around the ERG analytical result for each canister. Participants analyzed the canisters in replicate and reported both sets of analytical results. The canisters analyzed by the participants were analyzed on a variety of instruments, with a variety of analytical conditions. Samples were submitted to 37 PAMS, with 98 individual sets of data received. Each PAMS site was requested to perform and report two analyses (37 x 2=74 datasets). However, several PAMS sites elected to perform additional replicate determinations on additional instruments (12 x 2 = 24 additional datasets). The total of individual datasets was thus 74 + 24 = 98 datasets. Within 48 hours, PAMS were notified of the comparison of their analytical results to the ERG analytical results for the same canister. Approximately 30% of the returned canisters were re-analyzed by ERG on their return to the laboratory. Canisters selected for re-analysis generally had a major discrepancy between the ERG analysis and the external analysis. Four canisters were prepared and retained in the ERG laboratory to be analyzed again at the end of the study to provide information on the stability of the test compounds. The range of analytical results for the PAMS participants was wider than the range of the ERG analyses, but this result is to be expected since the ERG canisters were prepared in a short period of time and analyzed on one instrument over a short period of time. The results of the analysis can certainly be used by the PAMS to point out areas of the analytical procedure that can be improved.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

APPENDICES

LIST OF TABLES

Page

LIST OF TABLES (Continued)

Page

LIST OF FIGURES

Page

LIST OF FIGURES (Continued)

Page

LIST OF FIGURES (Continued)

Page

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

Page

EXECUTIVE SUMMARY

The Photochemical Assessment Monitoring Stations (PAMS) Quality Assurance (QA) Work Group requested Eastern Research Group (ERG) to work in conjunction with the States to conduct a performance evaluation program using audit canisters in order to assist the PAMS in assessing the quality of their analytical systems, and to assist the QA Work Group to evaluate the overall precision and accuracy of the National PAMS program. The two primary requirements for the proposed performance evaluation program were:

- That all ERG laboratory procedures be thoroughly documented so that canister concentrations of analytes provided to the participating States would be accurately known; and
- That feedback to the States reporting analytical results be rapid enough to allow them to repeat the analysis should they desire to resolve issues relating to analysis.

Eastern Research Group accordingly designed and performed a program consisting of the following components:

- Selecting and cleaning of canisters to be used for the program;
- Blanking canisters using Compendium Method TO-12;[1]
- Blanking canisters using gas chromatography/mass spectrometry with flame ionization detection (GC/MS-FID) for the analytes to be spiked;
- Preparing performance evaluation standards;
- Analyzing each performance evaluation standard by GC/MS-FID after preparation;
- Retaining at least three performance evaluation standard canisters in the ERG laboratories for a stability check;
- Checking final canister pressure before shipment;
- Shipping performance evaluation canisters with Instruction Sheet and Chain of Custody to the participants;
- Creating a database (Microsoft® Access) to track all information;

- Receiving duplicate results from participants;
- Responding with analytical results within 48 hours; and
- Compiling results and preparing a project final report.

Analytical results were received from the majority of the participants within two weeks of canister shipment. Several PAMS submitted analytical results from more than one analytical system when PAMS analyses were performed on more than one analytical system. Although participants were allowed to keep the performance evaluation canisters for a period of two weeks beyond the reporting of analytical results in order to repeat the analysis, if necessary, only one participant reported a repeated analysis.

Most of the reported results for the spiked compounds were within ±2 standard deviations of the ERG analytical results. There was only one set of points, duplicate points for propylene submitted by one participant, more than an order of magnitude out of the analytical range (± 2 standard deviations from the mean). These data points were rejected as outliers. The target compounds with the widest range of results were the very volatile compounds (C_2 hydrocarbons, negative bias of 10-15%) and the least volatile compounds (C_3-alkylbenzenes, positive bias ranging up to 10%). Decane showed the lowest bias, <1%. The group of compounds showing the lowest bias were the compounds eluting in close chromatographic proximity to the standard, propane. Compounds that were not reported (i.e., missed) were not treated as zeros in statistical calculations to avoid skewing data to low values.

In addition to a number of PAMS target compounds, four non-PAMS target compounds were also spiked into the performance evaluation canisters. These additional compounds provided a challenge to the compound identification procedures of several participants.

The most common compound identification errors were as follows:

- Methyl *t*-butyl ether was misidentified as 2,3-dimethylbutane or 2-methylpentane;

- 1-Hexene was misidentified as 2-methyl-1-pentene; and
- 1,1,1-Trichloroethane was misidentified as 2,4-dimethylpentane.

The use of non-PAMS target compounds in the standard mixture provided a useful evaluation of the identification and data validation procedures used by the participants.

1.0 INTRODUCTION

Ambient air quality surveillance regulations in Title 40 Part 58 of the Code of Federal Regulations (40 CFR Part 58)[1] include several provisions for enhanced monitoring of ozone (O_3) and its precursors including oxides of nitrogen (NO_x), volatile organic compounds (VOCs), including carbonyl compounds, and meteorological parameters. These revisions to the ambient air quality surveillance regulations require the States to establish Photochemical Assessment Monitoring Stations (PAMS). PAMS will be part of their existing State Implementation Plan (SIP) monitoring network in ozone nonattainment areas, and monitoring data must be reported to the U. S. Environmental Protection Agency (EPA). The additional ambient air pollutant and meteorological data are required because the National Ambient Air Quality Standards (NAAQS) have not been achieved for ozone. Additionally, a more comprehensive air quality database for ozone and its precursors is needed. The authority of the EPA for proposing the enhanced monitoring regulations stems from Title I, Section 182, of the Clean Air Act Amendments (CAAA) of 1990.

The monitoring stations for ozone and its precursors are identified as PAMS, with different types and frequencies of monitoring required on the basis of the population of the Metropolitan Statistical Area (MSA) or the Consolidated Metropolitan Statistical Area (CMSA). To assist the States in PAMS implementation, Technical Assistance Documents[2,3] have been prepared by EPA to address the siting of these monitoring stations and the sampling and analysis of ozone precursors.

The VOCs to be measured in the PAMS network are gaseous nonmethane organic compounds with a vapor pressure greater than 10^{-2} kilopascals, with a number of carbon atoms ranging from C_2 to C_{12}. These ozone precursors are saturated, unsaturated, cyclic, and/or aromatic hydrocarbons, as shown in Table 1-1. Some or all of these ozone precursors are expected to be found in ambient air. This list of compounds is listed in the Technical Assistance Document for Sampling and Analysis of Ozone Precursors.[3]

Table 1-1

Ozone Precursors

Ozone Precursors	
ethylene	3-methylhexane
acetylene	2,2,4-trimethylpentane
ethane	*n*-heptane
propylene	methylcyclohexane
propane	2,3,4-trimethylpentane
isobutane	toluene
1-butene	2-methylheptane
n-butane	3-methylheptane
trans-2-butene	*n*-octane
cis-2-butene	ethylbenzene
isopentane	*m*-/*p*-xylene
1-pentene	styrene
n-pentane	*o*-xylene
isoprene	*n*-nonane
trans-2-pentene	isopropylbenzene
cis-2-pentene	*n*-propylbenzene
2,2-dimethylbutane	*m*-ethyltoluene
cyclopentane	*p*-ethyltoluene
2,3-dimethylbutane	1,3,5-trimethylbenzene
2-methylpentane	*o*-ethyltoluene
3-methylpentane	1,2,4-trimethylbenzene
2-methyl-1-pentene	*n*-decane
n-hexane	1,2,3-trimethylbenzene
methylcyclopentane	*m*-diethylbenzene
2,4-dimethylpentane	*p*-diethylbenzene
benzene	*n*-undecane
cyclohexane	
2-methylhexane	Total Nonmethane Organic Compounds
2,3-dimethylpentane	

Note: *m*- and *p*-Xylene are listed together because of chromatographic coelution.

To identify the compounds and determine their concentrations, a sample of the ambient air must be collected, and the organic constituents concentrated and analyzed. The sample is typically cryogenically collected on a solid sorbent (preconcentration of organic compounds) and desorbed directly into an automated gas chromatograph for qualitative and quantitative analysis. Because there are a number of organic constituents of the ambient air, these constituents must be separated before analysis. Gas chromatography, using a capillary analytical column provides the best possible separation of the constituents prior to analysis. The quantitative analytical results are obtained by FID with gas chromatography. GC/FID relies upon chromatographic retention times for the identification of compounds.

The States are responsible for setting up and operating their own PAMS. A PAMS is successfully operated by collecting scheduled samples according to the regulatory requirements, analyzing samples according to accepted methodology, and reporting data to the appropriate regulatory agencies. Each state has an internal program to provide quality control and quality assurance. An external evaluation of the effectiveness of the PAMS analytical process (as assessed by an external performance evaluation sample) provides extremely valuable information regarding the successful operation of the PAMS. This external program was a performance evaluation rather than an audit, conducted primarily for the benefit of the monitoring organizations to allow the PAMS to evaluate how well they were performing their analyses. This report presents the specifications and procedures used in preparing, certifying, distributing, and managing a multiple-site performance evaluation program, with humidified performance evaluation samples prepared in 6-liter SUMMA®-polished stainless steel canisters.

1.1 PAMS Quality Assurance Work Group

A PAMS Quality Assurance Work Group, formed by the U. S. EPA, included representatives from EPA Office of Air Quality Planning and Standards (OAQPS), EPA National Exposure Research Laboratory (NERL), EPA Region II, EPA Region VI, Texas and California. The group was established to perform the following initial functions:

- Develop Quality Assurance and Quality Control procedures to be applied uniformly and inexpensively to raise the confidence levels of the field staff;

- Explore the development of Quality Assurance/Quality Control software (including error-checking, source profiles, and multi-variate techniques) for on-site integration at PAMS data collection locations (i.e., "real-time" Quality Assurance evaluations); and

- Provide information/reports to the Steering Committee and other work groups on the precision and accuracy of the PAMS data.

The Work Group tasked Eastern Research Group, Inc. (ERG) to supply performance evaluation samples to the PAMS. Performance evaluation samples supplied by an external laboratory are quality assurance tools that can be used to evaluate the precision and accuracy of an analysis. ERG was required to supply timely performance sample result information to the States in order to provide feedback that the participants could use to immediately improve their operations. The secondary purpose of this study was to assist the QA Work Group in evaluating the performance of the PAMS program as a whole and to help the EPA regions identify sites in need of additional assistance. In order to operate a successful performance evaluation program, it was essential to have accurate and precise measurement of the compounds in the performance evaluation samples which could be supplied to all of the participants at or very near the same time. In the event that problems were encountered, the PAMS had the opportunity to correct the problems and re-analyze the performance evaluation standard. In this project final report, the participants have the opportunity to evaluate their performance relative to other PAMS, although no specific identifications of the participants are made.

1.2 Performance Evaluation Canister Preparation Procedures

Humidified performance evaluation samples were prepared in 6-liter SUMMA®-polished stainless steel canisters and contained the compounds listed in Table 1-2. Twenty-two of the compounds listed in Table 1-2 are ozone precursors (see Table 1-1). Two additional

Table 1-2

Components of Certified Gas Cylinders

Cylinder 1	Cylinder 2
benzene	benzene
n-butane	1,3-butadiene
1-butene	cyclohexane
decane	ethylbenzene
ethane	ethylene
ethylbenzene	propylene
n-hexane	*tert*-butyl methyl ether
1-hexene	toluene
n-octane	1,1,1-trichloroethane
propane	1,2,3-trimethylbenzene
n-propylbenzene	1,2,4-trimethylbenzene
toluene	1,3,5-trimethylbenzene
	m-xylene
	o-xylene
	p-xylene

compounds included in the gas mixture are not ozone precursors. The performance evaluation samples were prepared in a single batch of forty canisters. (An additional batch of ten PE canisters was prepared when some of the original group of 40 were found to have leaked before shipment.) Prior to preparation of the performance evaluation samples, each canister was cleaned and certified for total nonmethane organic compound (NMOC) content to less than 10 ppbC. Each canister was also analyzed by GC/MS-FID to verify cleanliness on a compound-specific basis. The criterion for acceptable cleanliness of a canister was 1.0 ppbC or the detection limit for the specific compound, whichever is greater.

When the cleanliness of the canisters had been verified, performance evaluation samples were prepared from high pressure multiple-component gas cylinders obtained from a specialty gas manufacturer. The cylinders contained the compounds shown in Table 1-2, mostly hydrocarbons with carbon numbers from C_2 through C_{10} (analytical accuracy of ±5%), with some non-hydrocarbon volatile organic compounds also included. The canisters were prepared at a pressure of approximately 35 psig with a relative humidity of about 70%. The relative humidity was calculated based on the ideal gas law. The performance evaluation samples tested only the analytical portion of the PAMS procedures. To eliminate potential sources of variability or error in the analysis, the canisters were analyzed directly by the analytical system without the use of any slip-stream or pressure reduction devices.

Prior to distribution, each canister was analyzed by GC/MS-FID to verify the final composition and concentration. The concentration in ppbC of each component was referenced to a NIST-certified propane standard. The pressure of the canisters was also checked prior to shipment. Four additional canisters (baseline samples) were prepared and held by ERG for reanalysis and additional information on stability at the end of the program.

A database of all of the participants, the site locations, the bias of the performance evaluation results, and other relevant comments and information was created and maintained during the program using Microsoft Access®. A Chain of Custody form was created to track samples and collect other necessary information for the database.

Participants were requested to analyze the canister in replicate and, within two weeks, fax both sets of results to ERG. ERG compared the analytical results to the first set of analytical results generated by ERG and faxed a report to the PAMS within 48 hours. The participating PAMS could then reanalyze the canister, if desired, to resolve any performance issues, and return the canister to the ERG laboratory within one month. Once the canisters were returned to the ERG laboratory, a subset of the canisters was selected for reanalysis based on the results from the PAMS. The four reserved baseline canisters were also reanalyzed.

To ensure the success of the performance evaluation program, close coordination among EPA, ERG, and the site contacts was required, with timely reporting of results to the PAMS sites and reporting of technical progress and problems to the EPA.

2.0 CONCLUSIONS AND RECOMMENDATIONS

On the basis of ERG laboratory experience in performing and managing this program and the evaluation of the analytical results, the following conclusions are drawn:

- The compounds spiked into the performance evaluation canisters (Table 1-2) are stable in the canisters over a period of eight weeks: analysis at the beginning and at the end of the period shows minimal compound loss, both for canisters retained in the laboratory and for canisters shipped to the PAMS sites and returned to ERG.

- With the exception of compounds not reported (which were not included in statistical calculations), only two reported values were rejected statistically as outliers.

- The overall PAMS site average absolute value percent bias (considering only the magnitude of the bias, not the sign) was 11.31.

- The overall PAMS site average percent bias (considering that the bias can be positive or negative) was -0.25.

- After shipping the canisters to PAMS sites, where two or more analyses were performed, and returning the canisters to ERG, a second ERG analysis for sixteen canisters agreed with the initial ERG analysis generally within 10 percent.

- Providing rapid feedback to the PAMS is a crucial component of a successful program. With rapid feedback, the information provided by the evaluation can be applied immediately to solve PAMS analytical problems;

- For the highest reproducibility in preparation of performance evaluation standards, a certified cylinder (certified by the gas vendor) of gaseous standards should be used with dynamic flow dilution;

- Strong Quality Assurance and Quality Control procedures are essential in providing appropriate documentation for tracking the complete history of each performance evaluation canister;

- The majority of the participants were prompt, accurate, and precise in reporting their analytical data.

The following recommendations are made:

- To provide a good external check on laboratory procedures and build confidence in the program both internally and externally, performance evaluation samples should be provided on a regular schedule. Regularly-scheduled performance evaluation samples must also provide rapid feedback of results.

- To provide a challenge to the PAMS in compound identification procedures, the compounds to be spiked should be selected carefully. Including the complete PAMS target list should in general be avoided and including compounds extraneous to the PAMS target list is desirable.

- To provide a better test of the ability to perform quantitative measurements, standards should be prepared at different concentrations to produce a range of values. Some compounds should be spiked at concentrations close to actual ambient measurements and some compounds spiked at higher concentrations. Blending two certified cylinder standards at different concentrations would produce a range of values in the final performance evaluation standard.

- To get the best performance evaluation program possible, advance planning and an early start are necessary. Some delays are inevitable—funding is delayed, cylinder purchase may take longer than quoted by the suppliers, instruments and equipment need repair, etc. However, planning well ahead allows the program to compensate for delays.

All of these factors should be considered in planning a program for preparation and distribution of the performance evaluation standards.

3.0 LABORATORY PROCEDURES

The ERG laboratory procedures for preparation of performance evaluation standards consisted of four major parts:

- Cleaning canisters prior to preparation of audit samples;
- Verifying the cleanliness of the audit canisters by NMOC and by GC/MS-FID;
- Preparing diluted samples from high pressure multiple-component gas cylinders; and
- Verifying the final concentration and content of the audit canisters.

Procedures for each part of the operation are described.

3.1 Cleaning of SUMMA®-Passivated Stainless Steel Canisters

The canister cleaning procedure used for the performance evaluation standard canisters corresponds to the procedure described in the Technical Assistance Document.[3] The canisters are purged with cleaned humidified air and then subjected to high vacuum to ensure that the canister interior surfaces are free of contaminants. The canister must meet an NMOC cleanliness criterion of <10 ppbC (as measured by Method TO-12) to minimize the potential for carryover of organic pollutants from one sample to the next.

Complete and detailed records were maintained for each canister to track the cleaning procedure and each subsequent analysis to demonstrate cleanliness.

3.2 Verification of Cleanliness of the SUMMA®-Polished Canisters

The cleanliness of each canister was evaluated by using Compendium Method TO-12 procedures. The Method TO-12 blanking procedure requires a simple preconcentration procedure with subsequent analysis by direct flame ionization detection (PDFID) to provide an

accurate and precise measurement of total NMOC concentration, expressed as ppbC. When all cleaned canisters had met a Method TO-12 cleanliness criterion of NMOC<10 ppbC, GC/MS-FID was used to verify cleanliness on a compound-specific basis.

By convention, concentrations of NMOC are reported as parts per million carbon (ppmC). For this program, the criterion for cleanliness was 10 parts per billion carbon (ppbC). All canisters met this criterion.

3.3 Verification of Canister Cleanliness on a Compound-Specific Basis (GC/MS-FID Analysis)

Since a background level of one or more of the analytes would significantly bias the results of the performance audit, the cleaned blanked canisters were analyzed for speciated ozone precursors by GC/MS-FID.

The GC/MS-FID analytical system incorporates a sample concentration trap, a capillary gas chromatograph, a capillary column, a post-column splitter, and both a mass selective detector (MSD) and a FID. The FID is used to quantify the compounds of interest; the MSD is used to identify the compounds of interest. Moisture is removed from the analytical system using a permeable membrane drying device. The samples are cryogenically concentrated by using a trap consisting of chromatographic-grade stainless steel tubing packed with commercially available 60/80 mesh deactivated glass beads maintained at -185°C during sample concentration. The concentrated VOCs are thermally desorbed to revolatilize them for transfer to the analytical column for separation. All of the cleaned canisters met individual compound cleanliness criteria.

Analytical conditions are shown in Table 3-1.

Table 3-1

Analytical Conditions for GC/MS-FID Analysis of Ozone Precursor Compounds

Analytical System	
GC	Hewlett-Packard 5890 Series II
Mass Selective Detector	Hewlett-Packard 5971 MSD
Sample Concentration System	
Concentrator	NuTech, 16 valve autosampler
Chromatographic Conditions	
Column	J&W DB-1, 60 m x 0.32 mm, 1 µ film thickness
Carrier gas	Helium
Carrier Flow	1 mL/min
GC Program	-60°C for 5 min, then 6°C/min to 150°C, then 180°C for 8 min for a total run time of 50 min
MS Conditions	
Scan cycle	1 sec/scan, 5 min solvent delay
Electron voltage	70 eV, nominal

3.4 Preparation of Performance Evaluation Samples

Performance evaluation canister samples at a specific concentration (a concentration range of 10-50 ppbC) were prepared by dilution from cylinders containing the compounds shown in Table 1-2. The same procedure was used to prepare both the PAMS performance evaluation samples and GC/MS calibration standards.

Standards and performance evaluation samples were blended and diluted to the desired concentration with humidified air. A concentration of 25-50 ppbC per compound was targeted. The performance evaluation samples were prepared at a pressure slightly above 30 psig and a

relative humidity of about 70%. The canisters were pressurized to slightly above 30 psig since they would be opened for analysis in the ERG laboratory before being shipped at a pressure of 30 psig. The relative humidity was a calculated value based on the ideal gas law. To eliminate sources of error, the performance evaluation canisters were prepared to be ready for analysis, with no further dilution or preparation required. The canisters were shipped with a Chain of Custody (Figure 3-1) and a Letter of Instruction (Figure 3-2) to ensure that the history of the canister could be traced throughout the entire preparation and analysis process.

3.5 GC/MS-FID Analysis of Performance Evaluation Samples by ERG

Using the analytical procedure described above, each performance evaluation canister was analyzed once by GC/MS-FID to verify the composition and concentration prior to shipment. The ppbC concentration of each component in the canister was referenced to a NIST-traceable propane standard. Four additional performance evaluation standard canisters were retained in the ERG laboratory as baseline samples and held for reanalysis and for additional stability information at the end of the program. The interval between the two ERG analyses was approximately eight weeks: first analysis, 8/8/96; second analysis, 10/3/96.

The pressure of the performance evaluation standard canisters was checked immediately before shipment to ensure that participants would receive a canister at 30 psig. Five of the original batch of 40 canisters were found to have leaked. These canisters were rejected for shipment, and a second batch of ten performance evaluation canisters was prepared following the same procedures as were followed for the original batch of 40 canisters. The second batch of ten canisters was treated as a second data set.

ERG
EASTERN RESEARCH GROUP, INC.

Audit Data Sheet

Lab ID # _____ ***Can Serial #*** _____

Canister Cleaned:

Date: _____

Blank NMOC Analysis:

Date: _____ Analyst: _____

Blank GC/MSD Analysis:

Date: _____ Analyst: _____ Filename: _____

Standard Prep:

Date: _____ Analyst: _____ Humidity: _____ Pressure: _____

GC/MSD Analysis:

Date: _____ Analyst: _____ Filename: _____

Shipment:

Sent
Date: _____ Operator: _____ Fed Ex #: _____ Canister P (psig): _____

Received
Date: _____ Operator: _____ Fed Ex #: _____ Canister P (psig): _____

Lab Analysis:

First Analysis:
Date: _____ Analyst: _____ Filename: _____

Second Analysis:
Date: _____ Analyst: _____ Filename: _____

Note: If more than two analyses are done on the samples, please attach a page with explanation of results.

Shipment:

Sent
Date: _____ Operator: _____ Fed Ex #: _____ Canister P (psig): _____

Received
Date: _____ Operator: _____ Fed Ex #: _____ Canister P (psig): _____

Second GC/MSD Analysis:

Date: _____ Analyst: _____ Filename: _____

White: Original Copy Canary: Lab Copy Pink: Auditing Lab Copy Goldenrod: EPA Copy

Figure 3-1. Chain of Custody

PAMS QA Audit Sample Instructions

This canister contains a PAMS Performance Audit standard to be analyzed in your laboratory. Instructions for preparing the documentation are below.

1) Fill in the Received date, Operator, Fed Ex # and Canister Pressure (psig) under "Shipment" on the *Audit Data Sheet*.

2) Run each sample as received twice. **(NO FURTHER PREPARATION IS REQUIRED)**. If the samples are analyzed more than two times, please include these results and explanations on an attached sheet.

3) Fill in *Data Results Page*, complete with analytical conditions and results (in ppbC).

4) Fill in the Date, Analyst, and Filename on the *Audit Data Sheet* under the "Lab Analysis" for the First and Second Analysis. If more than two analyses were done on the sample, please provide this information on an attached page.

5) Fax the *Data Results Page* and a copy of the *Audit Data Sheet* to:

Julie Swift
Fax #: (919) 461-1579

6) the turn around time for sample results is two weeks (2 weeks) from date of receipt. Fax the data back by _____.

7) Fill in the Sent-Date, Operator, Fed Ex #, and Canister Pressure (psig) under "Shipment" on the *Audit Data Sheet*.

8) Send the canister back no later than _____ using the shipping information supplied.

If you have any questions, please contact either:

Julie Swift
Tel. (919) 461-1245

or

Joan Bursey
Tel. (919) 461-1334

Ship all canister, chain-of-custody, and hardcopy results to:

Shipping Address

Julie Swift
ERG
900 Perimeter Park, Dock C
Morrisville, NC 27560

Figure 3-2. Letter of Instruction

3.6 Analysis by PAMS

After completion of the GC/MS-FID analysis of the performance evaluation samples by ERG, the canisters were shipped, with custody documentation, to the PAMS. The PAMS in general analyzed the canisters in replicate within two weeks of receipt according to their analytical procedures, and both sets of results were faxed to ERG. The ERG laboratory compared the results to the analytical results obtained for that canister prior to shipment and a report was faxed to the site contact at the PAMS. The PAMS had the option of repeating the analysis of the performance evaluation canister after data were received from ERG. However, only one PAMS exercised the option to repeat the analyses.

3.7 Preparation of a Database of PAMS Results

A database of the participants, site locations, result bias, and other relevant comments and information was created using MicroSoft® Access. The custody documentation and the form used in sample tracking contributed information to the database. The information generated by the PAMS (the replicate results for the analysis of the performance evaluation canister) was entered into the database and verified to ensure that no transcription errors were made. The database is available to EPA at the conclusion of the study.

3.8 Repeated Analysis of Performance Evaluation Samples

Upon completion of analysis at the PAMS the canisters were shipped back to ERG. When the canisters were received at the ERG, some of the total number of canisters returned (approximately 30%) were selected for re-analysis based on the PAMS analytical results. The results from the repeated analysis were added to the database. The four baseline canisters retained at ERG were also re-analyzed.

3.9 Quality Control Information

The laboratory quality control procedures used at ERG are summarized in Table 3-2.

The minimum requirement of a laboratory quality control program is an initial demonstration of laboratory capability and an ongoing analysis of internal audit standards to evaluate and document data quality. Laboratory records are used to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet performance requirements. When analytical results of audit samples indicate atypical performance for the analytical method, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation for the analytical instrumentation.

Before processing any samples, a blank sample is analyzed to demonstrate that interferences from the analytical system are under control. The blank samples for this program consisted of a clean canister of clean humidified air which, under analysis, demonstrated that no analytes were observed above the detection limit.

The tune of the GC/MS system to meet *p*-bromofluorobenzene specifications was verified every 12 hours. An initial multipoint calibration was performed to meet laboratory acceptance criteria. A daily calibration check standard was analyzed on all analytical instruments to verify that the chromatographic systems were operating properly. The chromatographic profile was examined to ensure that adequate chromatographic properties and resolution were being maintained by the analytical system. Consistency between the response of the analytical system to the calibration check standard was evaluated on a day-to-day basis to ensure that instrument sensitivity was maintained. Response factors generated from analysis of the daily calibration check standard were compared to the mean response factors generated by the analysis of the multipoint calibration to verify the stability of the GC/MS system. Standard signal levels were monitored on a run-to-run basis to demonstrate the stability of the analytical system.

Table 3-2

Summary of PAMS Performance Evaluation Quality Control Procedures

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
System Blank Analysis	Daily, following calibration check, prior to analysis	1.0 ppbC or Method Detection Limit, whichever is greater for target compounds	1) Repeat analysis. 2) Check system for leaks
Five-point calibration for propane (five concentrations) for both MS and FID, bracketing the expected sample concentration	Monthly	Correlation coefficient (r) $\geq$ 0.995 RSD of response factors < 30%	1) Repeat individual sample analysis 2) Repeat linearity check 3) Prepare new calibration standards and repeat
Calibration check using mid-point of calibration curve	Daily (every 12 hours) on the days of sample analysis	Response within ±30% difference of calibration curve slope	1) Repeat check 2) Repeat calibration curve
Canister cleaning certification	All canisters prior to sample preparation	$\leq$10 ppbC total	1) Reclean canister and repeat analysis

On the FID and TO-12 analytical systems, a daily check standard (NIST-certified propane) is analyzed to verify the stability of the analytical system. A multipoint calibration was performed monthly and checked daily to verify that the calibration is still valid and meets acceptance criteria.

Quality control procedures applied to this program include:

- Adequately-trained personnel;
- Supervision to ensure that the Quality Assurance Project Plan was followed;

- Documentation of experimental results in dedicated project notebooks in a manner that will facilitate reconstruction of project activities and verification of data accuracy;

- Review of the progress of the work by senior technical reviewers and independent Quality Assurance staff to assess the effectiveness of the internal quality control program;

- Use of traceable standards and accurately prepared test substances;

- Use of equipment that is calibrated and tested according to laboratory Standard Operating Procedures;

- Documenting routine and non-routine maintenance of analytical instrumentation to allow an assessment of reliability;

- Following sample and data labeling procedures to help prevent sample and data mix-ups; and

- Testing quality control samples to assess the appropriateness of the analytical system and sample preparation instrumentation.

3.9.1 Precision

The precision of the preparation of the performance evaluation canisters was determined from the GC/MS-FID analysis of each prepared standard. The precision objective for the entire batch of performance evaluation canisters was a variation of less than 10% relative standard deviation. This objective was achieved for all of the compounds except ethane (precision, as measured by relative standard deviation, was 21.19%). Ethane also failed to meet the 10% relative standard deviation in the second batch of canisters (precision, as measured by relative standard deviation, was 13.54%). This variability in the measurement resulted in a broadening of the range for analyses of ethane.

The standard deviation (SD) of the ERG measured values for the performance evaluation samples was determined for each analyte using the following equation:

$$SD = \left[\frac{\sum (X_i - X_{avg})^2}{n - 1} \right]^{1/2}$$

where:

n = number of determinations

X_{avg} = mean of n determinations

X_i = i^{th} value

$$RSD=CV = \frac{SD}{X_{avg}} \times 100$$

where:

RSD = relative standard deviation

CV = coefficient of variation

The standard deviations of the measured values for the PAMS were calculated in the same way. The measured value for each compound in each PAMS performance evaluation canister was expressed as ERG measured value ± 2δ, where δ = SD.

3.9.2 Bias

The bias (B) of each of the replicate results submitted by the PAMS was calculated for each analyte using the following equation:

$$\%Bias = \frac{\text{Measured Value} - \text{True Value}}{\text{True Value}} \times 100$$

where:

Measured Value = Value measured by the PAMS

True Value	=	Value measured by ERG for each compound in each canister prior to shipment of the canister.

The percent bias was determined and reported individually for each of the replicate values reported by the PAMS.

The bias between the theoretical value for each analyte in the canister and the ERG measured value was also calculated.

3.9.3 Completeness

The quality assurance objective for completeness was 100 percent, with no samples invalidated because they were damaged or lost. This objective was achieved with respect to damage or loss of samples. All canisters shipped were received by the PAMS participants in acceptable condition for analysis. The projected data set was not complete, however, since analytical results were not reported from one laboratory that received a canister.

4.0 RESULTS AND DISCUSSION

The performance evaluation canisters were prepared and analyzed by ERG in two batches prior to shipment to the participants. An initial batch of 40 canisters was prepared and analyzed, with the results for this set of data presented in Tables 4-1 (Theoretical Amounts) and 4-2 (Analyzed Amounts).

4.1 Analysis Results

Cylinder contents were not analyzed directly (without dilution) prior to preparation of the diluted canisters because the undiluted cylinder gas concentration was too high for the analytical system.

With isolated exceptions, ERG analyzed values for the canisters show a low bias relative to the theoretical/calculated values, indicating that the concentrations of the compounds in the cylinders have become lower over time. The low bias is greatest in magnitude for ethane and for the least volatile compounds (decane and later-eluting compounds). Ethane and the other compounds less volatile than decane also showed the largest range (analytical mean ± 2 standard deviations) in the analysis. The wide range for ethane is very different from the narrow range and low bias shown for ethylene, also a C_2-hydrocarbon. Theoretical and analytical results for all performance evaluation standards prepared, both the initial batch of 40 and the second batch of ten, are shown in Appendix E.

The consistent negative bias for the late-eluting compounds may represent cylinder loss or may represent a reproducible laboratory error such as an inadequately heated transfer line. Since the bias was very reproducible, a cause was not pursued.

Table 4-1
Original Batch of Forty Canisters: Theoretical/Calculated Amounts

Compound	Theoretical Value (Mean)[1]	Range[2]	Median[3]	90% Confidence Limits[4]	90th Percentile[5]
benzene	77.42	76.82-78.02	77.38	0.08	77.69
n-butane	27.82	27.60-28.04	27.81	0.03	27.92
1-butene	27.82	27.60-28.04	27.81	0.03	27.92
cyclohexane	35.59	35.15-36.03	35.55	0.06	35.69
n-decane	69.55	69.01-70.09	69.51	0.07	69.79
ethane	14.47	14.35-14.59	14.46	0.01	14.52
ethylbenzene	99.91	99.11-100.71	99.86	0.10	100.26
ethylene	11.92	11.82-12.02	11.91	0.01	11.96
n-hexane	41.73	41.41-42.05	41.71	0.04	41.87
n-octane	55.64	55.20-56.08	55.61	0.06	55.83
propane	20.86	20.70-21.02	20.85	0.02	20.94
n-propylbenzene	62.60	62.12-63.08	62.56	0.06	62.81
propylene	17.66	17.52-17.80	17.65	0.02	17.72
toluene	90.39	89.69-91.09	90.34	0.09	90.70
1,2,3-trimethylbenzene	52.82	52.40-53.24	52.79	0.05	53.00
1,2,4-trimethylbenzene	51.58	51.18-51.98	51.55	0.05	51.76
1,3,5-trimethylbenzene	49.71	49.33-50.09	49.68	0.05	49.88
m-/*p*-xylene	87.71	87.03-88.39	87.65	0.09	88.00
o-xylene	51.32	50.92-51.72	51.29	0.05	51.49

Table 4-1
Continued

[1] Value calculated from nominal cylinder values and dilution factors.
[2] Range = (mean ERG theoretical value for benzene in 40 canisters) ± 2 standard deviations, for benzene, the mean of the ERG theoretical values for all 40 canisters is 77.42, with a standard deviation of 0.30. Range therefore equals 2(0.30)-77.42 + 2(0.30) = 76.82-78.02.
[3] Median of 40 theoretical values.
[4] A confidence interval is a range on either side of a sample mean used to estimate the population mean with a specified probability. For small sample size (usually less than 100), the confidence interval is calculated as follows:

$$\text{Confidence Interval} = \text{MEAN}_s \pm t_{(1-\alpha/2,n-1)} \times \left(\frac{\text{STD}_s}{\sqrt{n}} \right)$$

where:

Confidence Interval = the range for the estimate of the population mean for the specified probability, 1-α (for a 95% probability level, 1-α=0.95 and therefore α=0.05)

MEAN_s = the sample mean

$t_{(t-\alpha/2,n-1)}$ = the two-sided t-value for the specified probability (1-α) and degrees of freedom (n-1)

n = the sample size

[5] Percentile establishes a threshold of acceptance, i.e., the values that would be above the 90th percentile.

Table 4-2

Original Batch of Forty Canisters: ERG Analyzed Values

Compound	Analyzed Value (Mean)[1]	Range[2]	Median[3]	90% Confidence Limits[4]	90th Percentile[5]	% Bias (Analyzed vs. Theoretical) (Mean)
benzene	69.80	66.66-72.94	70.13	0.40	71.33	- 9.84
n-butane	27.97	26.35-29.59	27.89	0.21	28.94	0.54
1-butene	25.82	22.82-28.82	26.03	0.38	27.42	-7.19
cyclohexane	32.38	30.94-33.82	32.52	0.18	33.22	- 9.02
n-decane	53.41	43.33-63.49	54.92	1.29	57.65	-23.21
ethane	10.10	5.82-14.38	9.58	0.55	13.29	-30.20
ethylbenzene	83.56	8.48-88.64	84.28	0.65	85.68	-16.36
ethylene	11.04	9.28-12.80	11.15	0.22	11.52	-7.38
n-hexane	9.60	37.38-41.82	39.76	0.29	40.45	-5.10
n-octane	9.33	46.93-51.73	49.69	0.31	50.39	-11.34
propane	21.55	20.49-22.61	21.53	0.14	22.22	3.31
n-propylbenzene	49.85	44.17-55.53	50.61	0.73	51.71	-20.37
propylene	16.65	15.73-17.57	16.65	0.12	17.23	-5.14
toluene	5.80	72.26-79.34	76.26	0.46	77.55	-16.14
1,2,3-trimethylbenzene	38.17	30.91-45.43	38.97	0.93	40.31	-27.73
1,2,4-trimethylbenzene	38.76	32.46-45.06	39.49	0.81	40.71	-24.85
1,3,5-trimethylbenzene	39.80	34.42-45.18	40.48	0.69	41.37	-19.94
m-/*p*-xylene	74.66	69.08-80.24	75.24	0.72	77.47	-14.88
o-xylene	39.36	36.52-42.20	39.78	0.36	40.28	-23.30
Total NMOC	861.42	804.20-918.64	867.51	7.35	885.52	

Table 4-2

Continued

[1] Value calculated from nominal cylinder values and dilution factors.
[2] Range = (mean ERG theoretical value for benzene in 40 canisters) ± 2 standard deviations, for benzene, the mean of the ERG theoretical values for all 40 canisters is 77.42, with a standard deviation of 0.30. Range therefore equals 2(0.30)-77.42 + 2(0.30) = 76.82-78.02.
[3] Median of 40 theoretical values.
[4] A confidence interval is a range on either side of a sample mean used to estimate the population mean with a specified probability. For small sample size (usually less than 100), the confidence interval is calculated as follows:

$$\text{Confidence Interval} = \text{MEAN}_s \pm t_{(1-\alpha/2,n-1)} \times \left(\frac{\text{STD}_s}{\sqrt{n}} \right)$$

where:

Confidence Interval = the range for the estimate of the population mean for the specified probability, $1-\alpha$ (for a 95% probability level, $1-\alpha=0.95$ and therefore $\alpha=0.05$)

MEAN_s = the sample mean

$t_{(t-\alpha/2,n-1)}$ = the two-sided t-value for the specified probability ($1-\alpha$) and degrees of freedom (n-1)

n = the sample size

[5] Percentile establishes a threshold of acceptance, i.e., the values that would be above the 90th percentile.

After the performance evaluation canisters were analyzed by ERG, the canisters were given a final pressure check and shipped to the PAMS participants together with a Chain of Custody form and an Instruction sheet. When the pressure of the canisters was checked prior to shipment, five canisters had leaked. While the leaking canisters were being repaired, the standards were re-prepared and re-analyzed in other leak-free canisters, and the performance evaluation samples were shipped to arrive at the participating laboratories as soon as possible after ERG analytical verification.

The PAMS participants analyzed the performance evaluation samples according to their own procedures and reported the results to ERG. ERG compared the analytical results to the reference analytical results generated by ERG and faxed a report to the participants within 48 hours. Analytical results included the ERG range (mean ERG analytical value ± 2 standard deviations), percent bias for each analysis relative to the ERG analyzed value for that canister, and the bias between the two reported results. Some laboratories performed a second and even a third set of replicate analyses on different analytical systems. Individual results for each analysis are shown in Appendix A. A representative set of results is shown in Table 4-3.

Combined results for all of the PAMS are shown in Appendix B. In Appendix B, every individual set of results submitted by each laboratory is considered a data set. There were 98 sets of individual results. Calculated statistical parameters for the entire set of results submitted by the PAMS are summarized in Table 4-4.

A compound-specific comparison of ERG and PAMS analytical results is shown graphically in Figures 4-1 through 4-19. By far the highest degree of scatter in the analyses, as illustrated by the percent coefficient of variation, is shown by propylene. The graph for propylene (Figure 4-20) shows two points (replicate analyses on the same analytical system) that are more than an order of magnitude higher than all of the other analyses. A histogram of all of the laboratory results (Figure 4-21) illustrates that these two data points are statistical outliers. When these two outliers for propylene are omitted from the data set, the correspondence between ERG and PAMS results is far closer (Figure 4-22).

Table 4-3

Example Reported Dataset for a PAMS Site

Compound	Analysis 1	Analysis 2	ERG Range[1]	% Bias 1	% Bias 2	Precision
ethylene	7.70	7.70	9.60-13.10	-32.16	-32.16	0.00
ethane	11.00	10.70	14.42-14.64	-24.29	-26.36	0.21
propylene	14.60	14.50	16.15-17.99	-14.49	-15.08	0.07
propane	17.80	17.40	21.33-23.45	-20.49	-22.27	0.28
1-butene	27.90	27.50	22.83-28.83	8.02	6.48	0.28
n-butane	29.00	28.60	27.41-30.67	-0.13	-1.51	0.28
n-hexane	37.50	37.80	37.61-42.07	-5.87	-5.11	0.21
benzene	66.90	66.60	67.67-73.99	-5.56	-5.98	0.21
cyclohexane	32.10	31.80	31.37-34.23	-2.15	-3.06	0.21
toluene	70.10	70.40	73.60-80.68	-9.12	-8.73	0.21
n-octane	46.70	47.00	47.98-52.80	-7.31	-6.72	0.21
ethylbenzene	79.80	81.30	80.56-90.72	-6.82	-5.07	1.06
m-/*p*-xylene	72.10	73.30	71.14-82.28	-6.01	-4.44	0.85
o-xylene	38.30	38.90	37.75-43.43	-5.64	-4.17	0.42
n-propylbenzene	50.50	50.80	45.89-57.27	-2.10	-1.52	0.21
1,3,5-trimethylbenzene	38.90	39.00	36.46-47.22	-7.02	-6.78	0.07
1,2,4-trimethylbenzene	37.50	38.20	34.82-47.42	-8.81	-7.11	0.49
n-decane	51.80	52.50	46.84-67.01	-9.01	-7.78	0.49
1,2,3-trimethylbenzene	38.60	39.40	33.55-48.07	-5.42	-3.46	0.57
Total NMOC	831.20	836.20	829.93-944.39	-6.31	-5.74	3.54

[1] ERG range = ERG analyzed value for this compound in this canister ± 2 standard deviations for this compound in the ERG dataset.

Table 4-4

Statistical Evaluation of Results Obtained from All PAMS[1]

Compound	Mean	Std. Dev.[2]	CV %[3]	Median	Conf. Lts.[4] 90%	90th Pct.[5]
ethylene	9.72	3.67	37.76	10.50	0.62	12.48
ethane	12.03	4.31	35.83	13.40	0.73	15.20
propylene	21.73	32.22	148.27	17.52	5.47	19.84
propane	20.83	3.21	15.41	20.65	0.54	23.62
1-butene	25.60	7.12	27.81	27.32	1.21	31.05
n-butane	28.63	3.75	13.10	28.35	0.64	32.00
n-hexane	41.08	8.18	19.91	41.80	1.39	47.22
benzene	74.62	11.23	15.05	75.65	1.91	85.48
cyclohexane	34.22	5.14	15.02	34.06	0.87	38.93
toluene	84.27	10.64	12.63	84.60	1.81	94.60
n-octane	53.99	5.93	10.98	54.62	1.01	62.02
ethylbenzene	94.30	13.70	14.53	95.11	2.32	106.61
m-/*p*-xylene	80.36	17.50	21.78	84.27	2.97	95.31
o-xylene	43.99	6.32	14.37	44.55	1.07	49.80
n-propylbenzene	56.36	12.23	21.70	57.95	2.07	65.07
1,3,5-trimethylbenzene	43.31	7.06	16.30	44.17	1.20	50.26
1,2,4-trimethylbenzene	42.65	10.67	25.02	44.19	1.81	52.05
n-decane	52.66	22.59	42.90	59.10	3.83	70.73
1,2,3-trimethylbenzene	39.62	17.10	43.16	44.00	2.88	53.43
Total NMOC[6]	958.32	120.06	12.53	960.98	20.37	1086.55

[1] Total of 98 sets of data (37 participating PAMS sites x 2 analyses per site) = 74 sets of data. Some sites performed additional sets of duplicate determinations, 12 additional determinations x 2 datasets per determination = 24 additional datasets. Total datasets=74+24=98.
[2]Standard deviation.
[3]Coefficient of variation
[4]Confidence Limits (90%)
[5]90th percentiles
[6]Total NMOC represents 94 data sets. All laboratories did not report a value for Total NMOC.

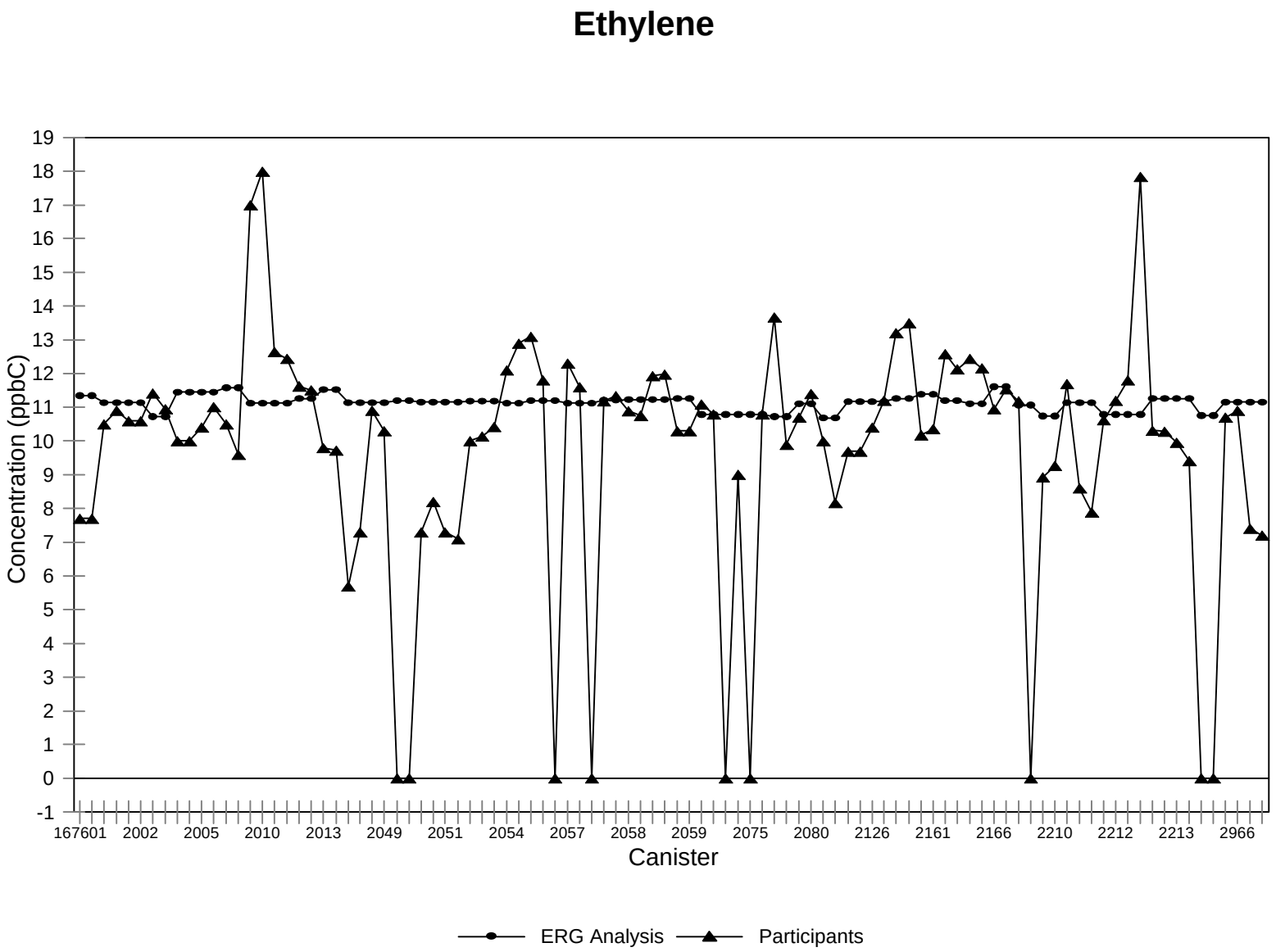

Figure 4-1. Graphical Comparison of Analytical Results for Ethylene Between ERG and Participants

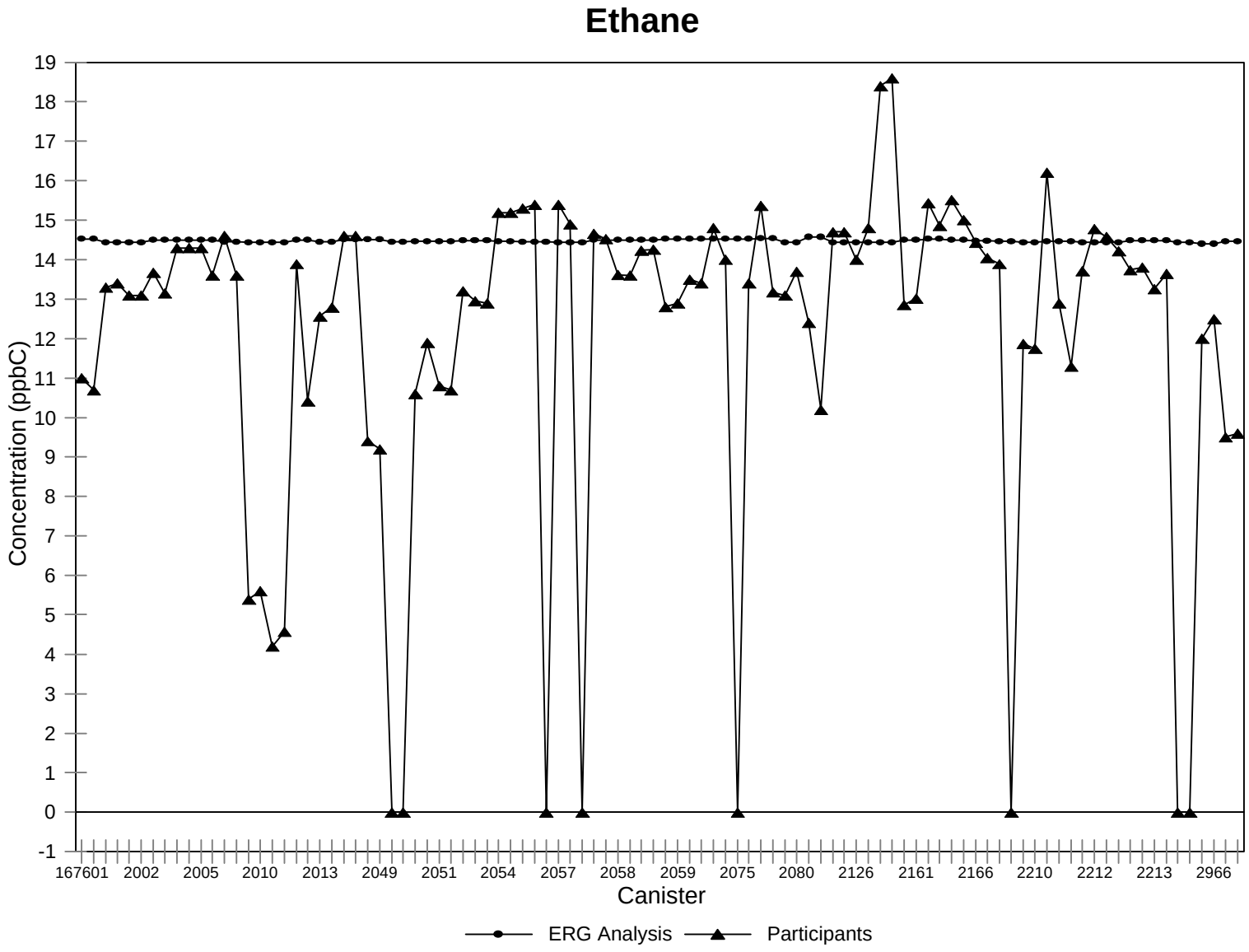

Figure 4-2. Graphical Comparison of Analytical Results for Ethane Between ERG and Participants

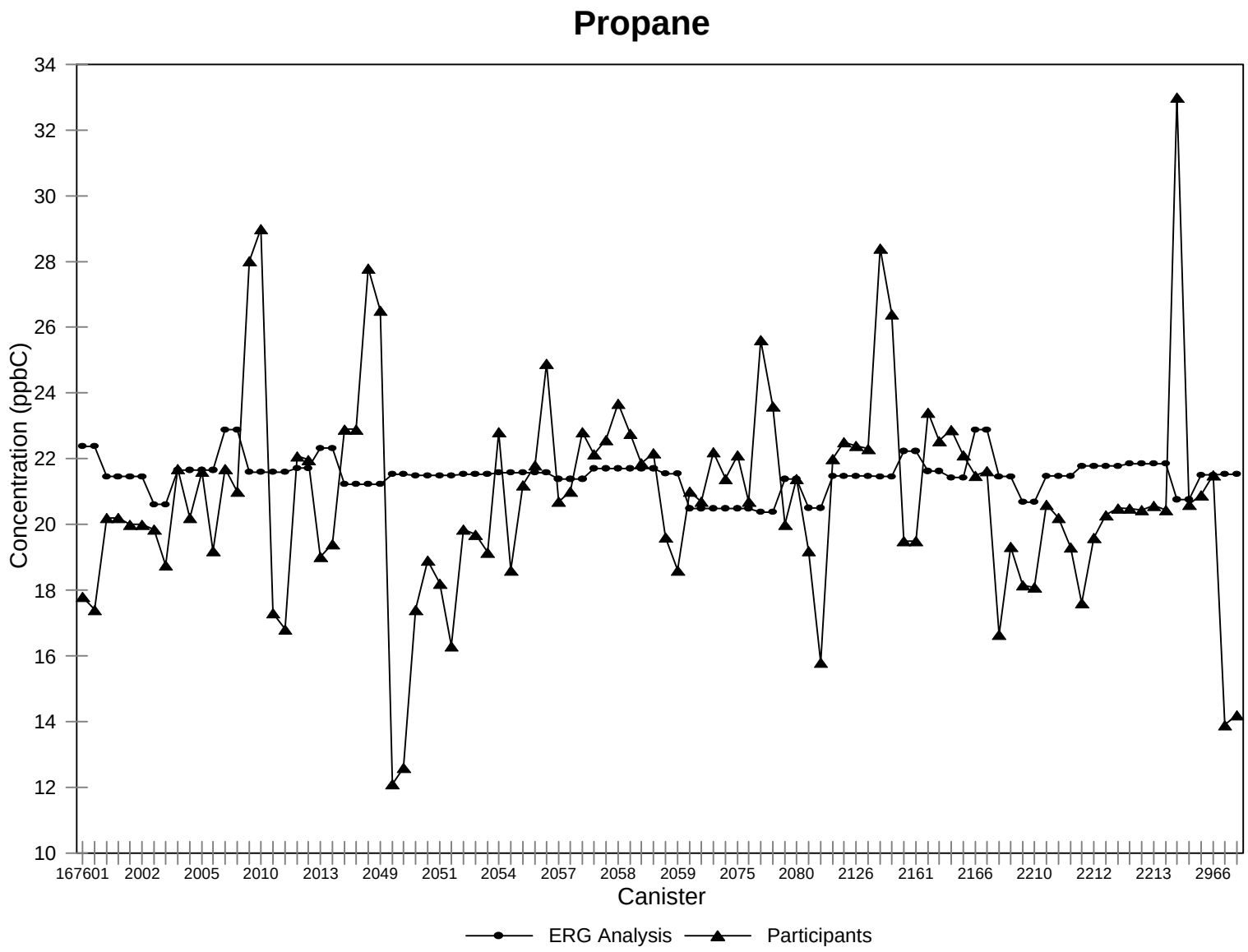

Figure 4-3. Graphical Comparison of Analytical Results for Propane Between ERG and Participants

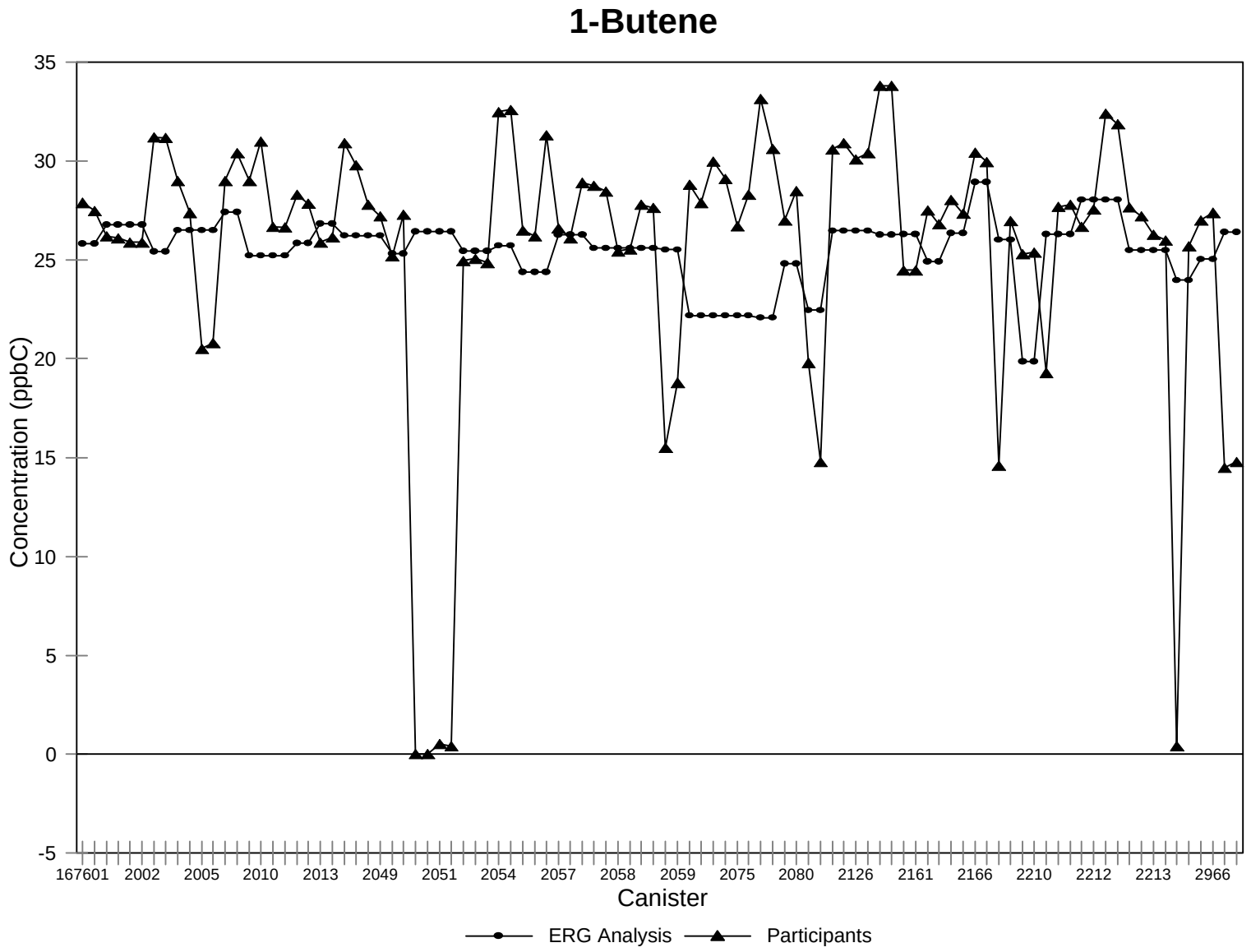

Figure 4-4. Graphical Comparison of Analytical REsults for 1-Butene Between ERG and Participants

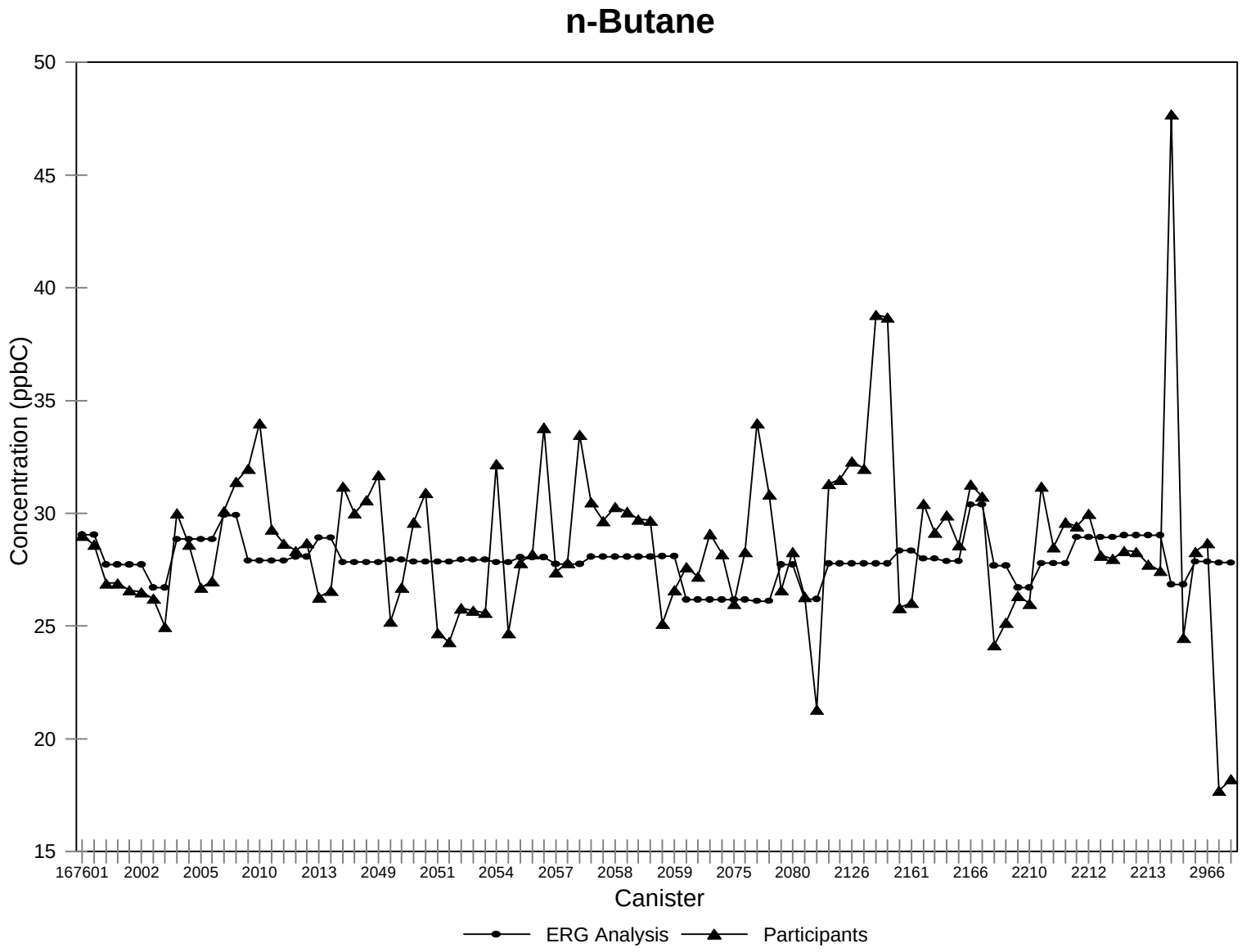

Figure 4-5. Graphical Comparison of Analytical Results for *n*-Butane Between ERG and Participants

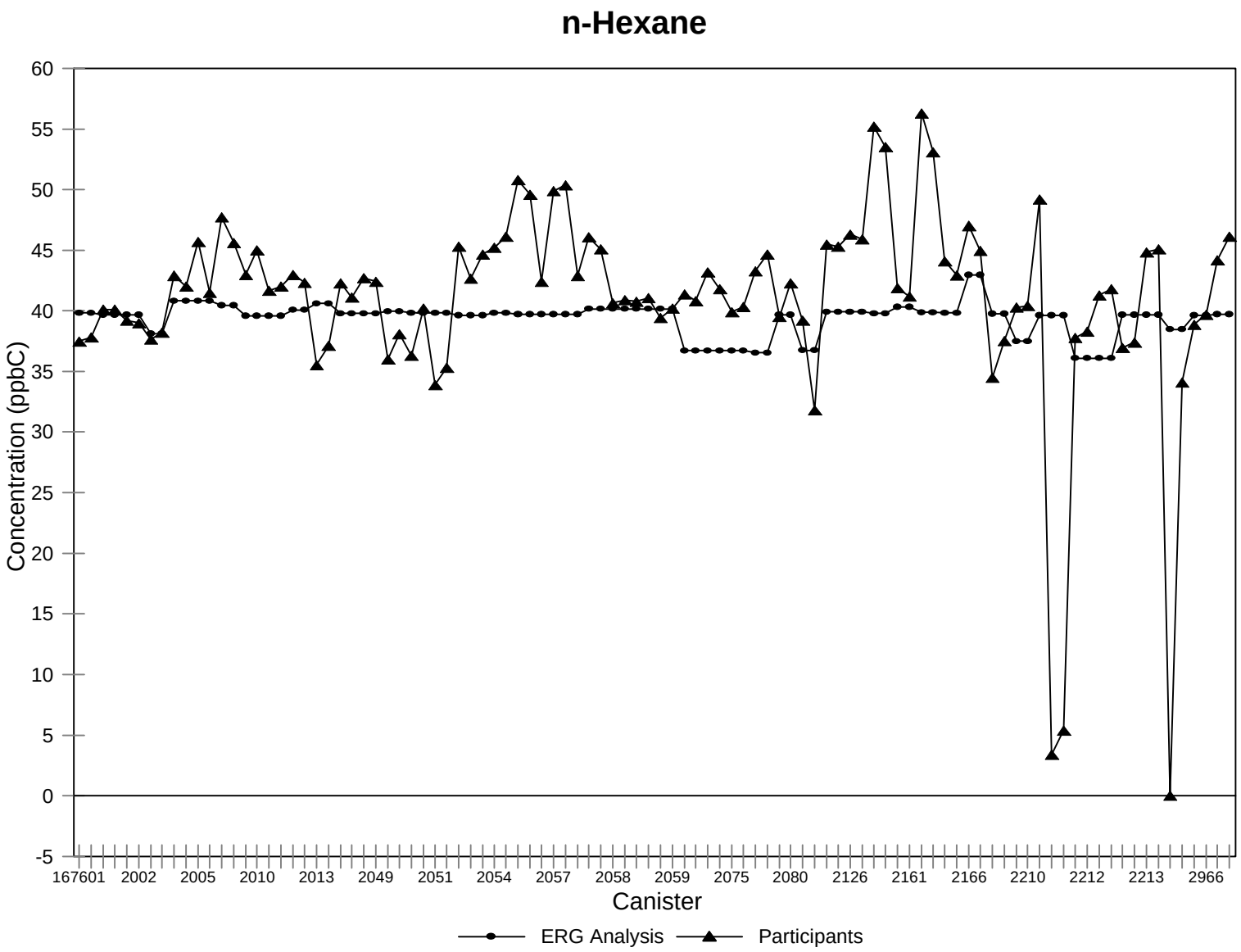

Figure 4-6. Graphical Comparison of Analytical Results for *n*-Hexane Between ERG and Participants

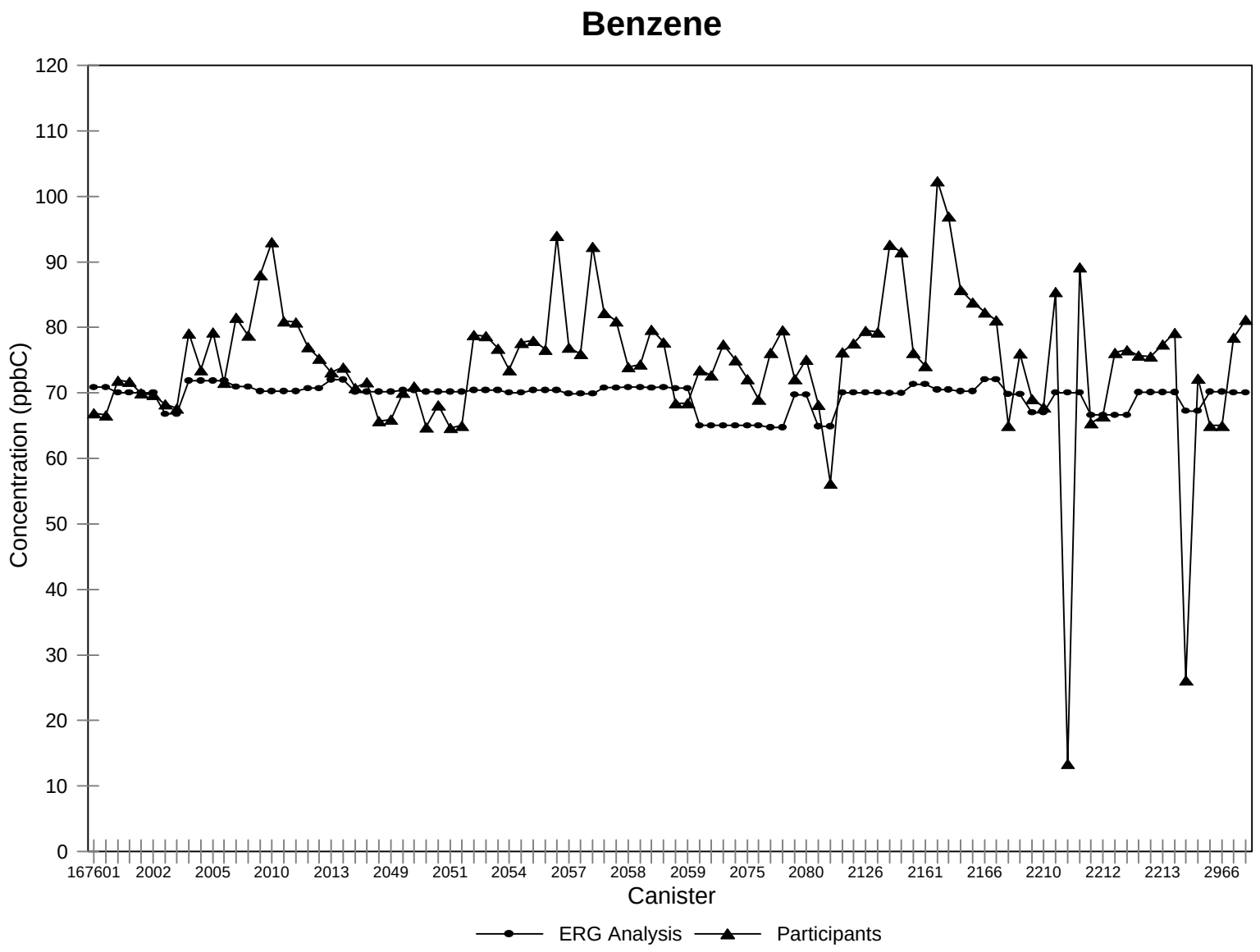

Figure 4-7. Graphical Comparison of Analytical Results for Benzene Between ERG and Participants

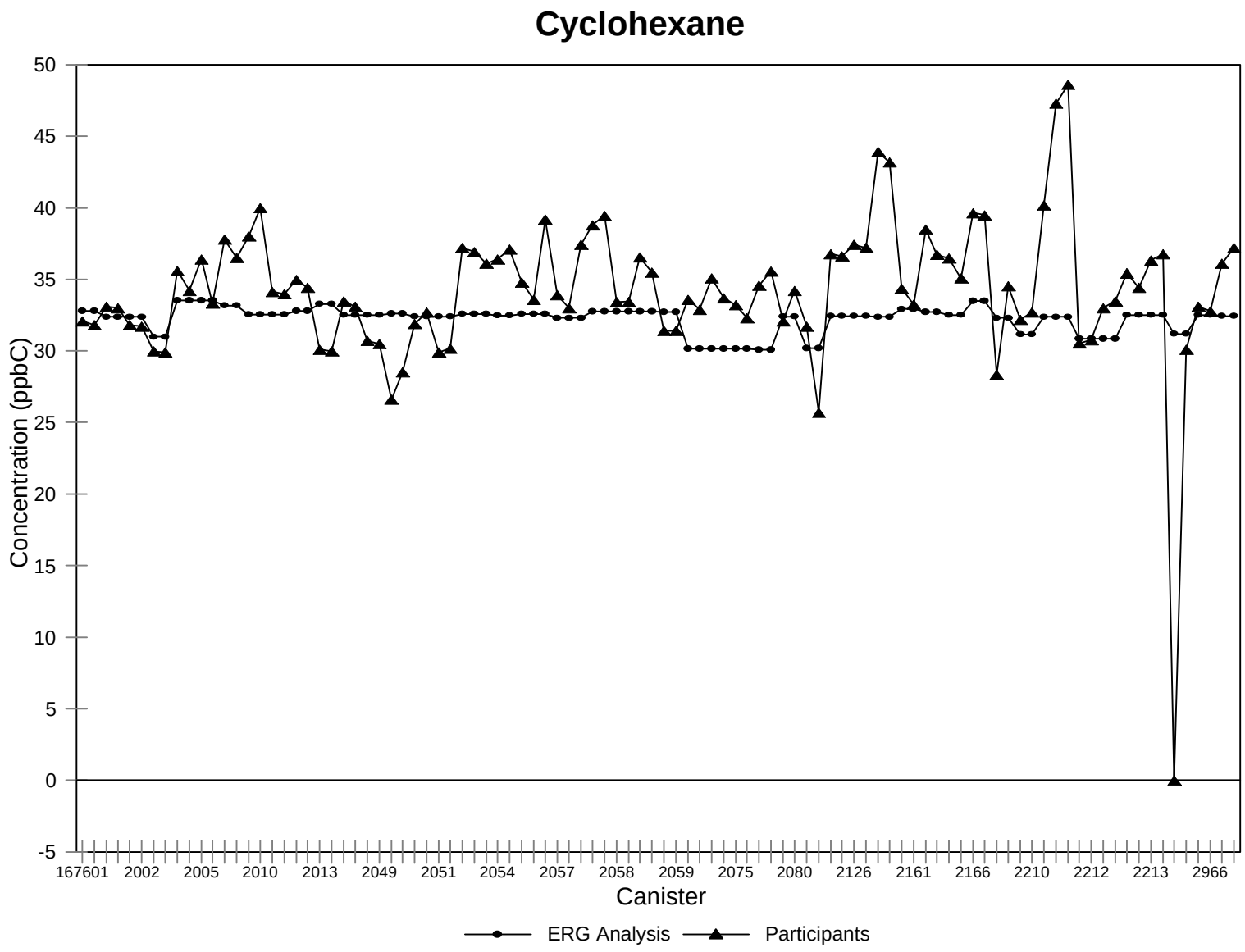

Figure 4-8. Graphical Comparison of Analytical Results for Cyclohexane Between ERG and Participants

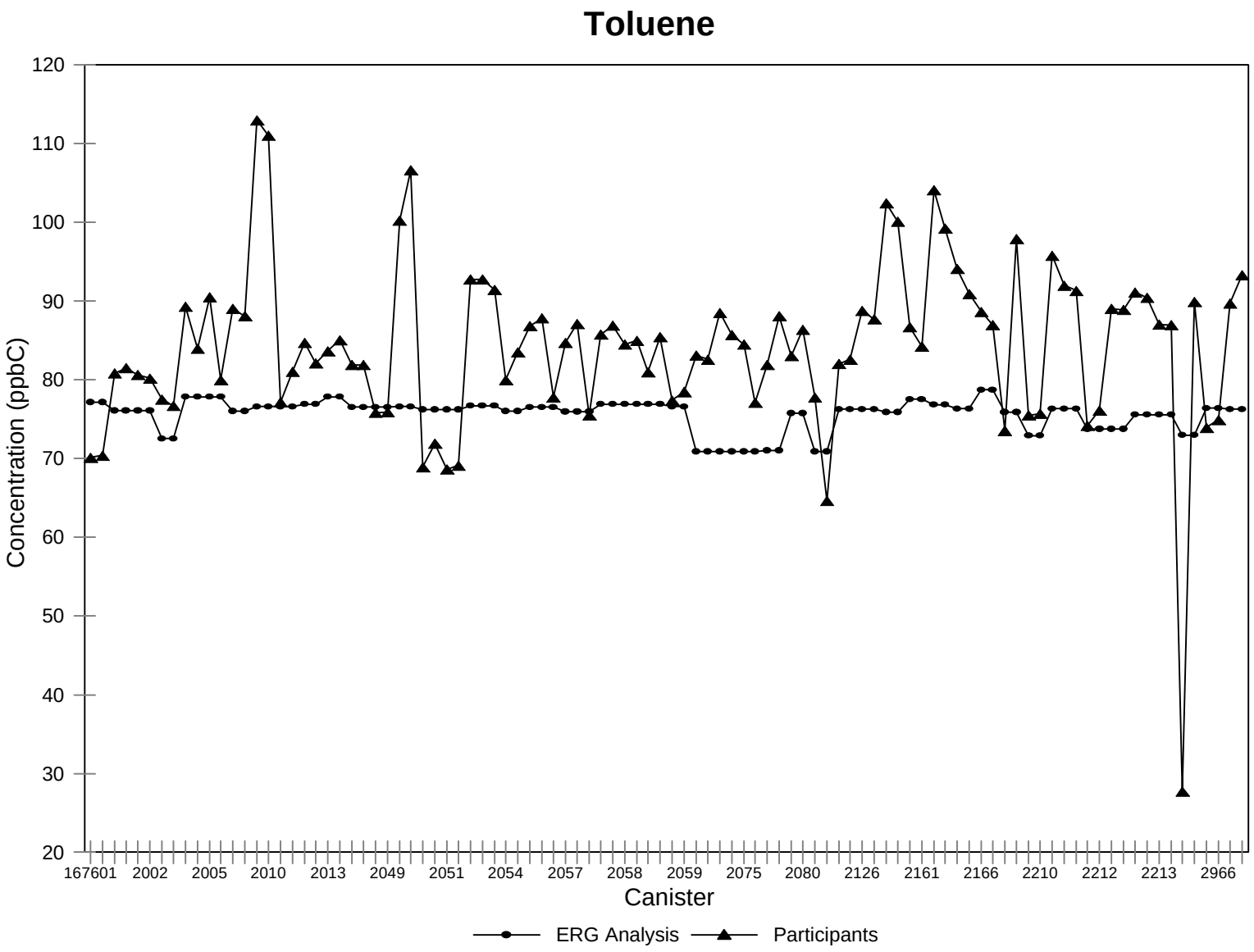

Figure 4-9. Graphical Comparison of Analytical Results for Toluene Between ERG and Participants

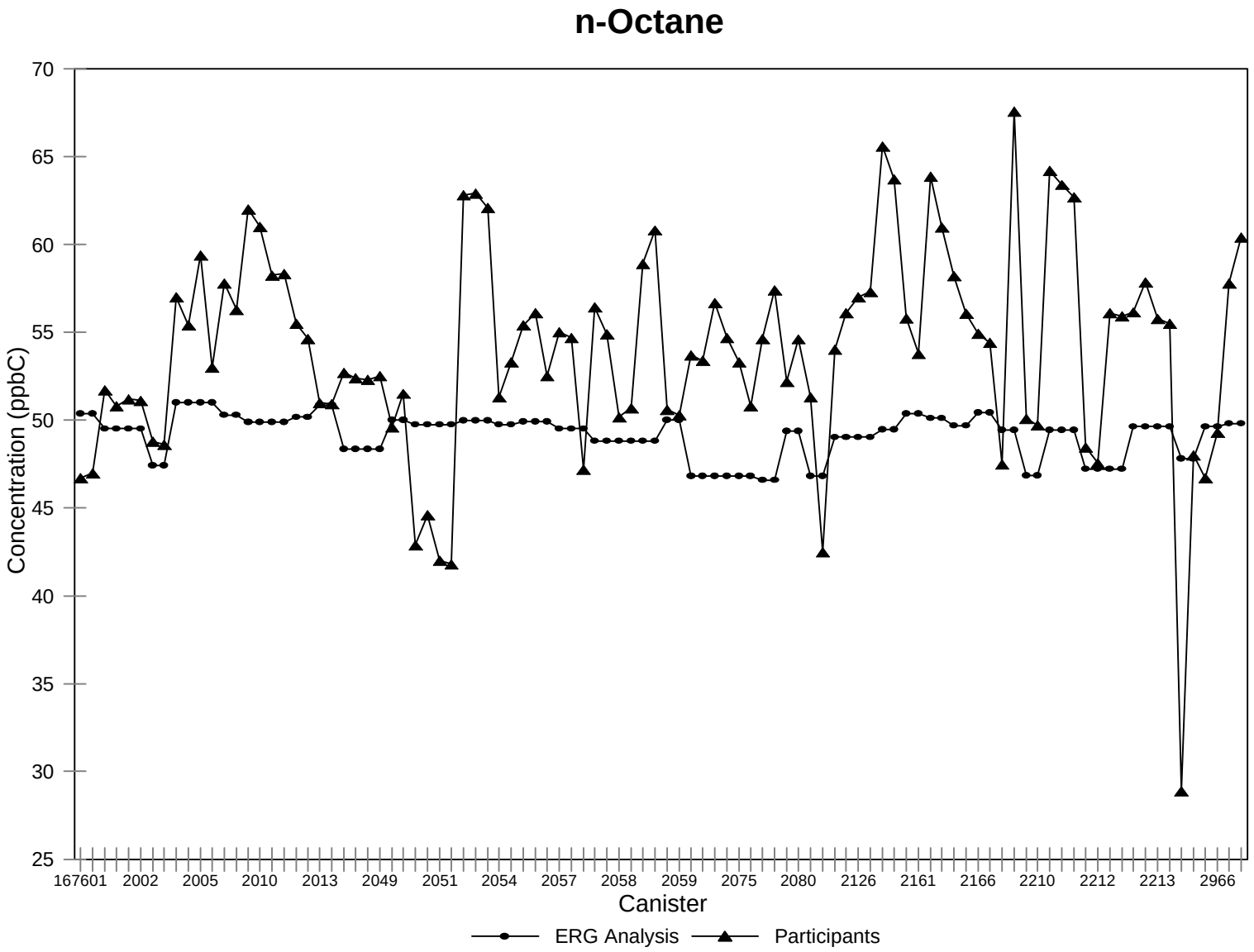

Figure 4-10. Graphical Comparison of Analytical Results for *n*-Octane Between ERG and Participants

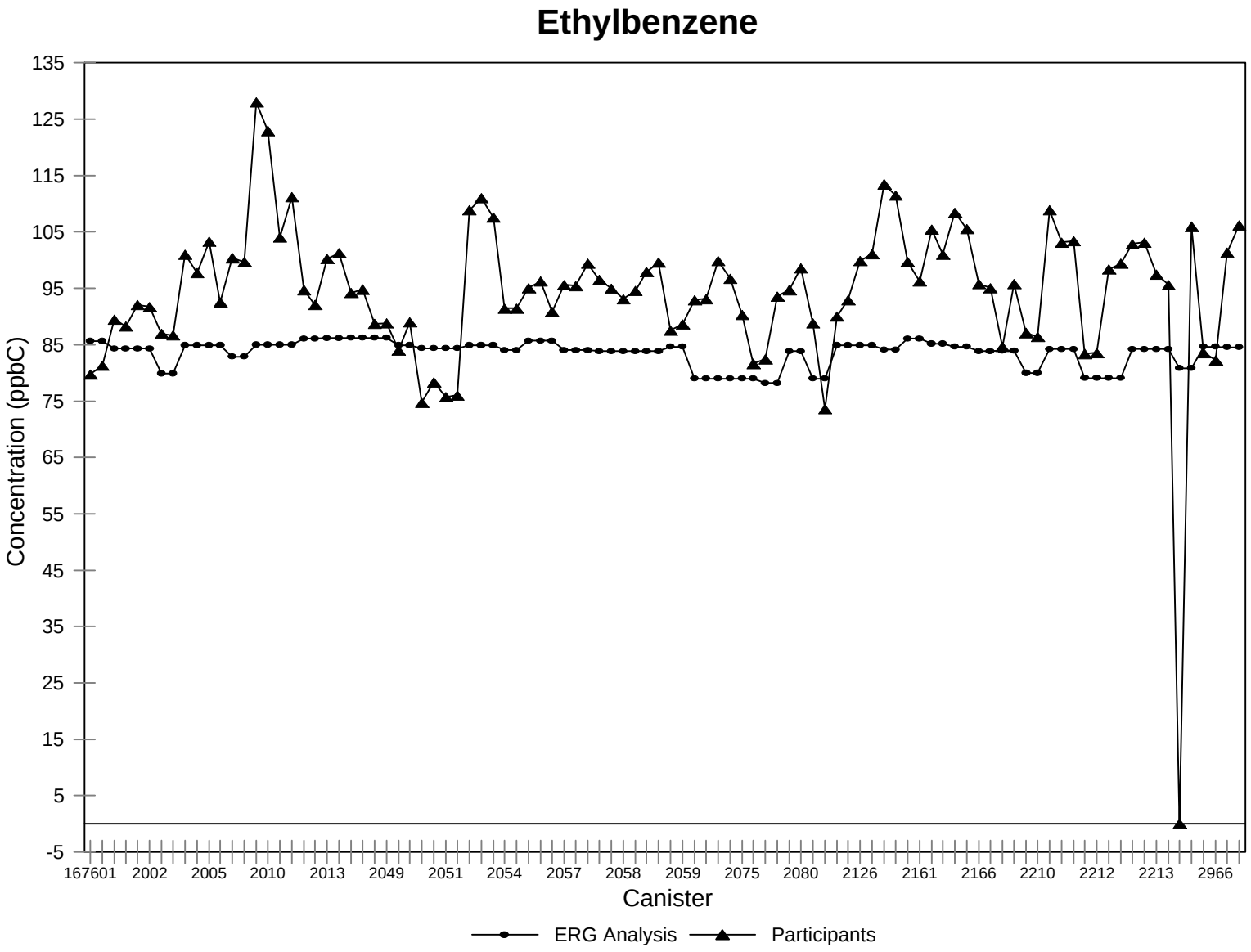

Figure 4-11. Graphical Comparison of Analytical Results for Ethylbenzene Between ERG and Participants

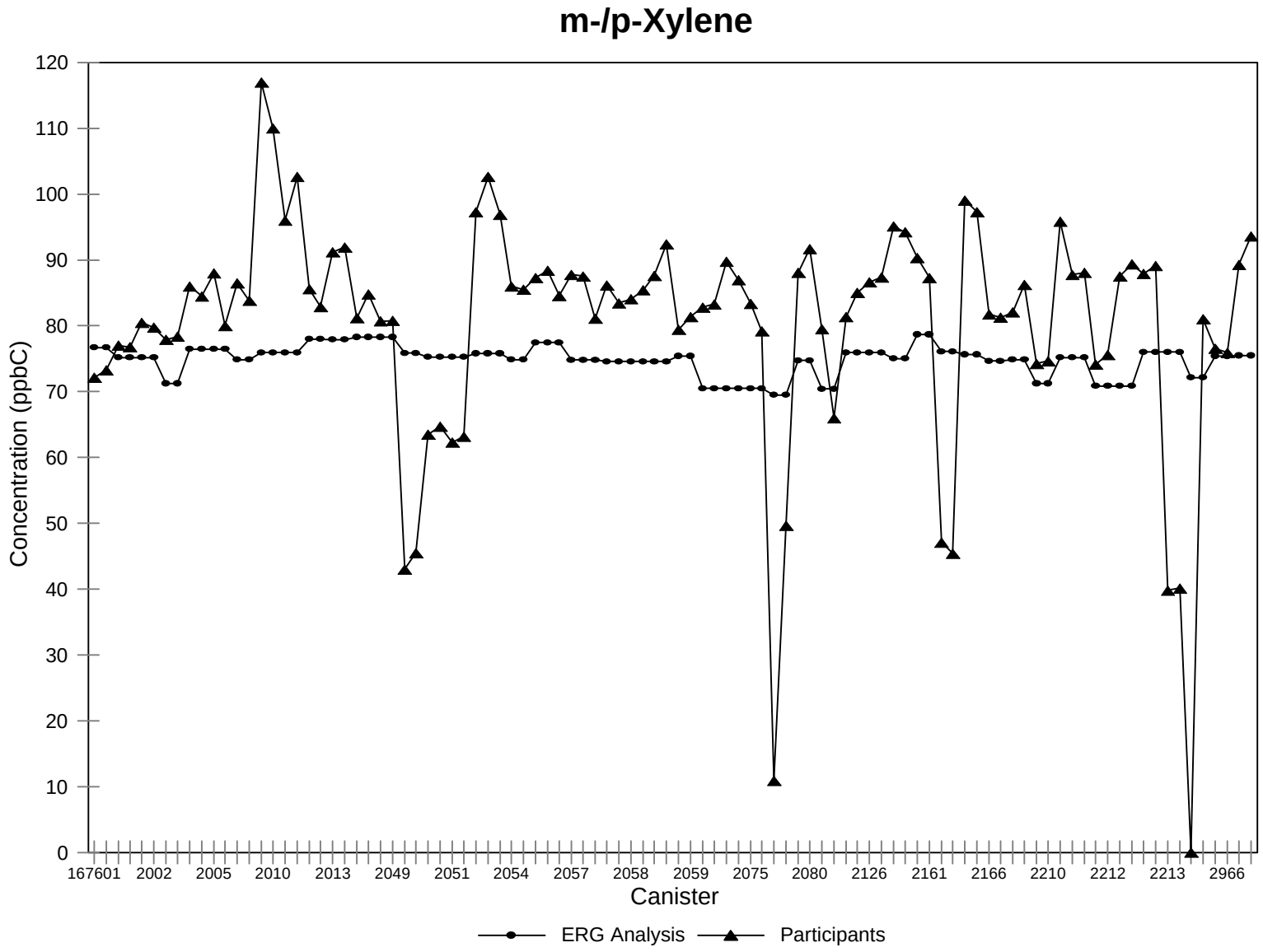

Figure 4-12. Graphical Comparison of Analytical Results for *m*-/*p*-Xylene Between ERG and Participants

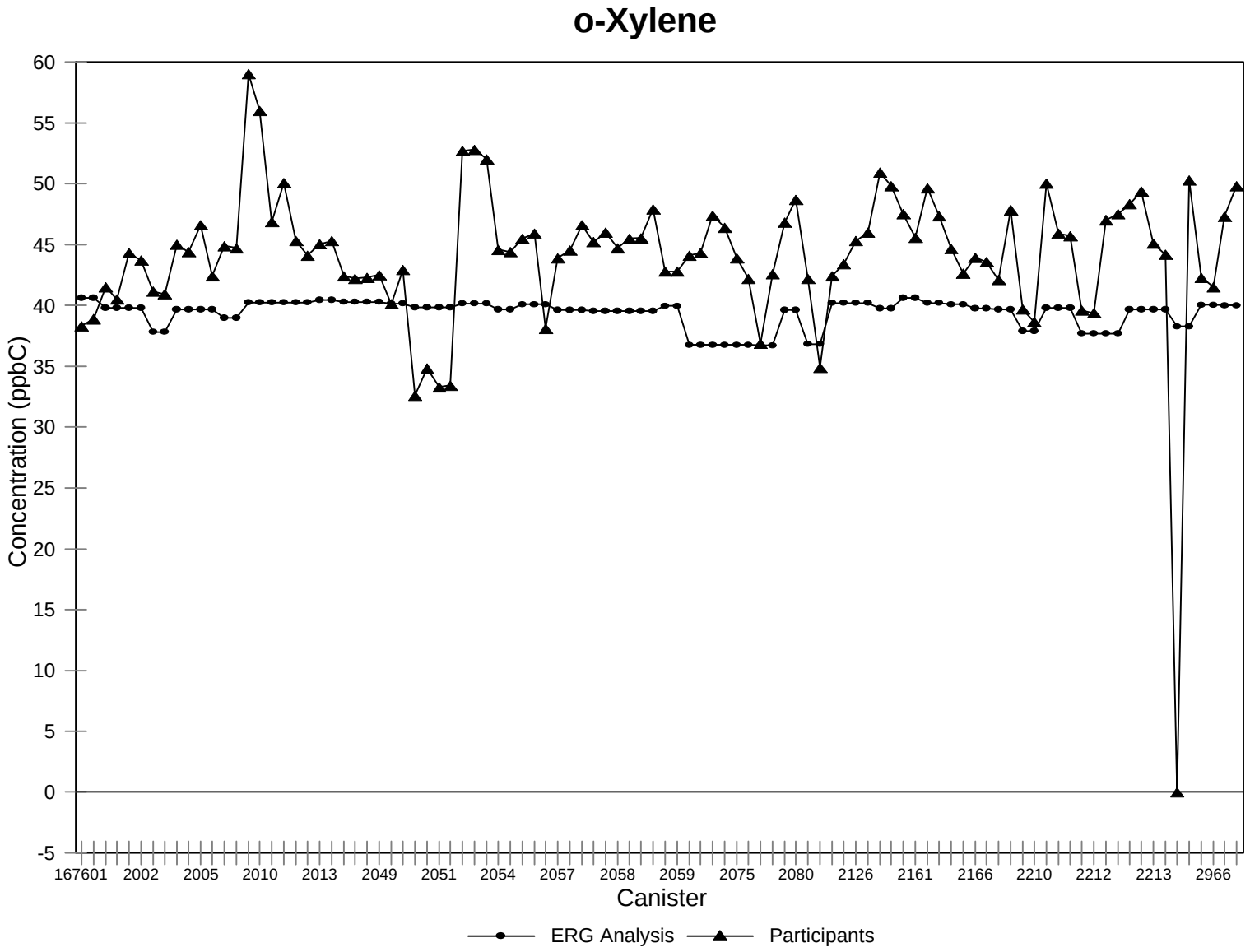

Figure 4-13. Graphical Comparison of Analytical Results for *o*-Xylene Between ERG and Participants

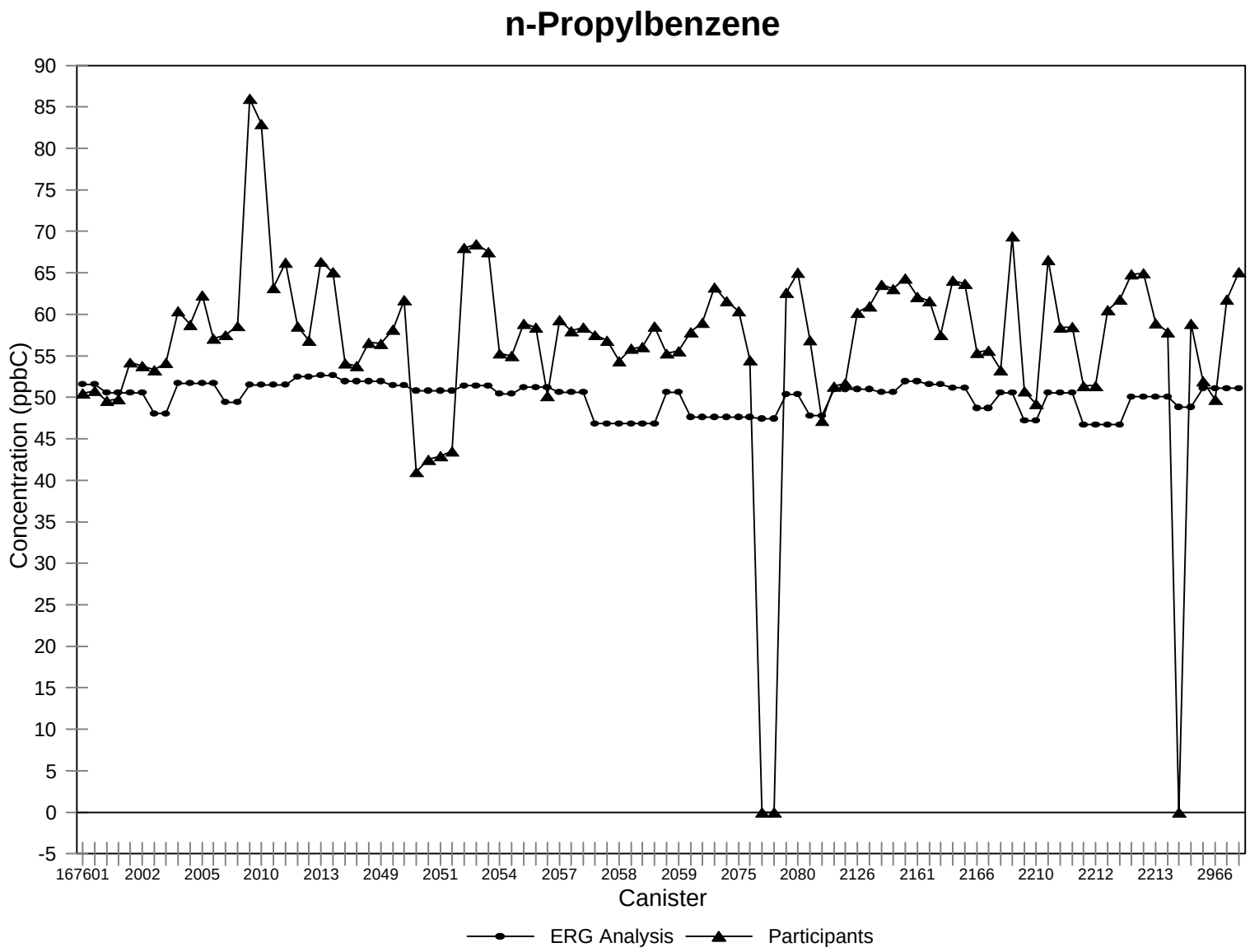

Figure 4-14. Graphical Comparison of Analytical Results for *n*-Propylbenzene Between ERG and Participants

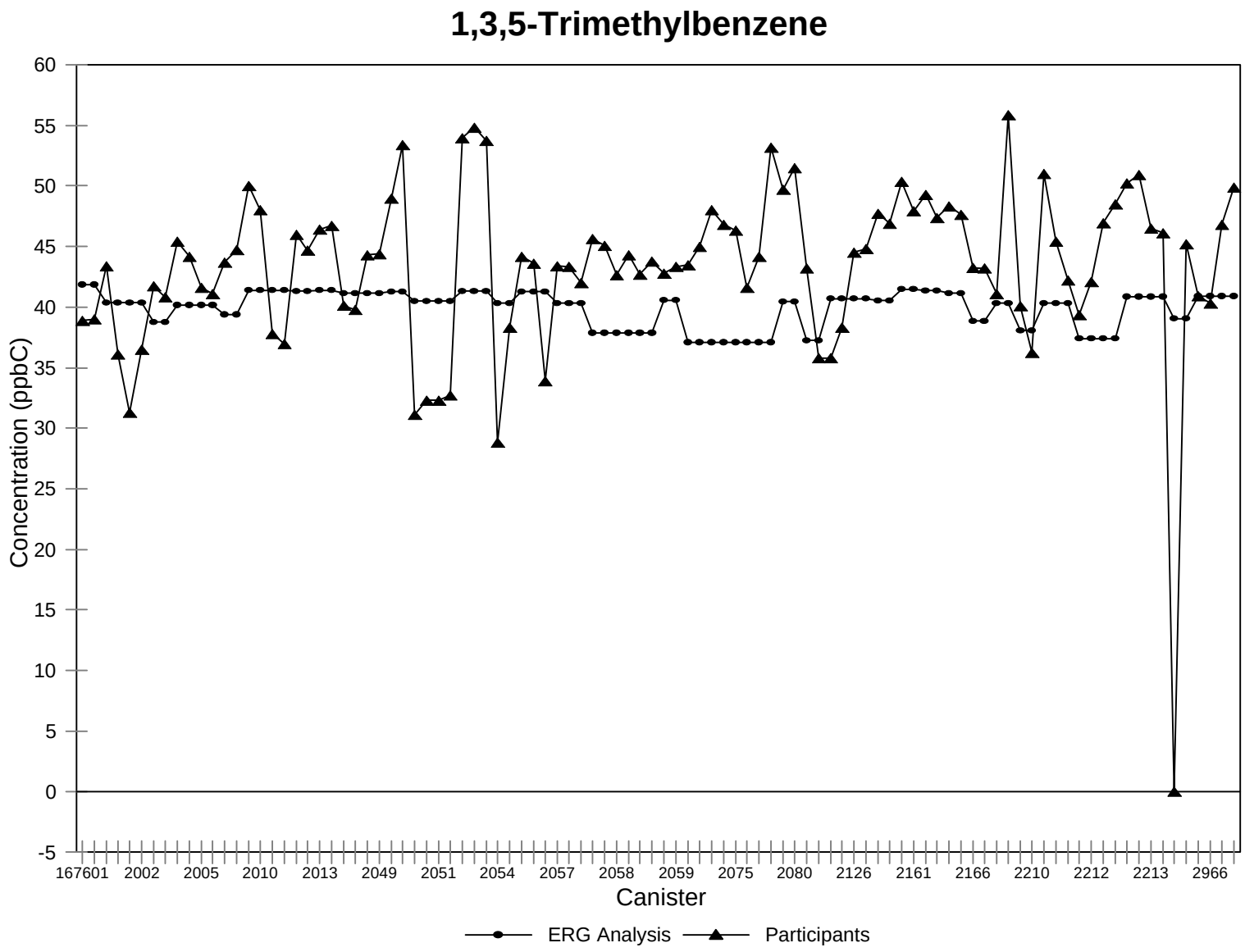

Figure 4-15. Graphical Comparison of Analytical Results for 1,3,5-Trimethylbenzene Between ERG and Participants

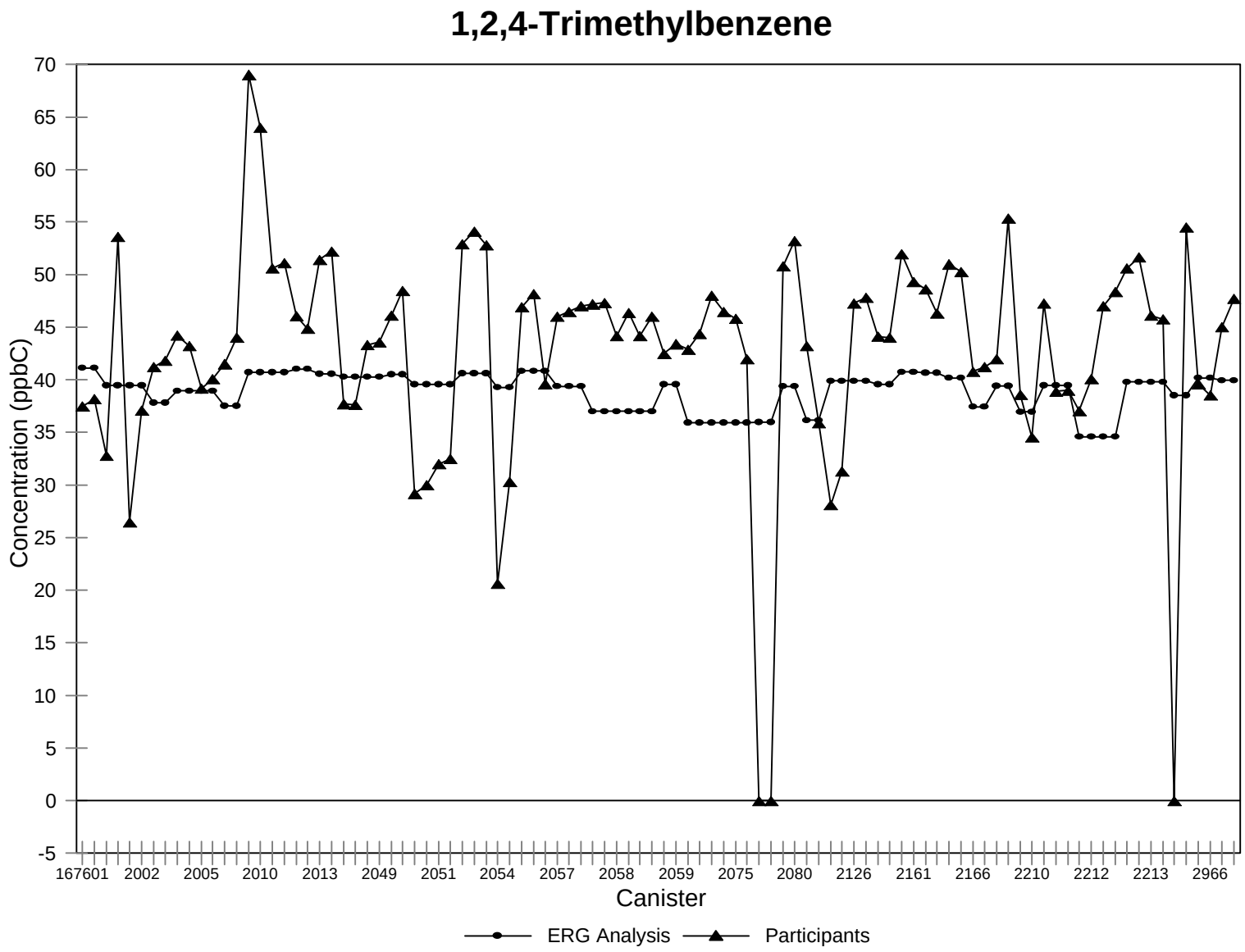

Figure 4-16. Graphical Comparison of Analytical Results for 1,2,4-Trimethylbenzene Between ERG and Participants

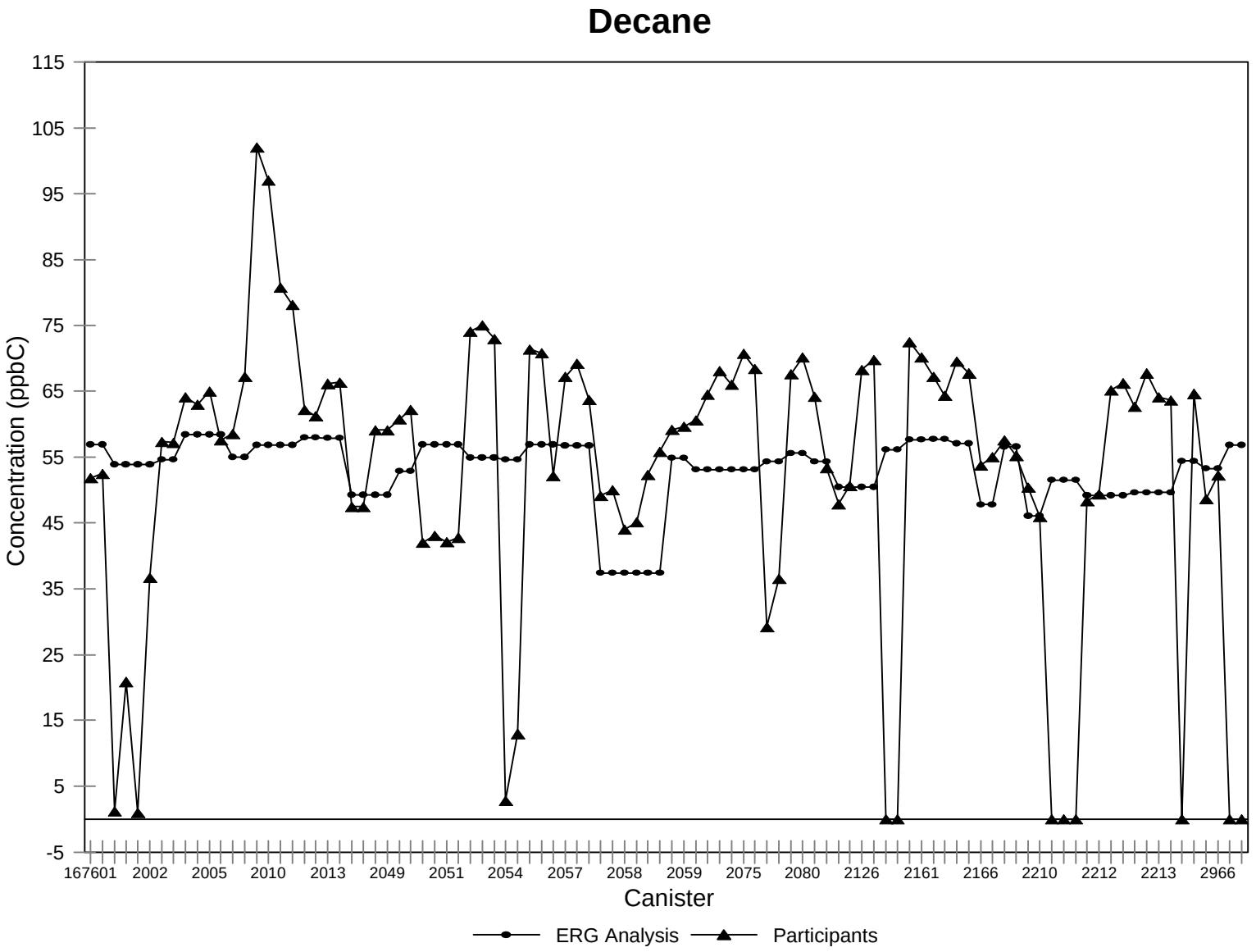

Figure 4-17. Graphical Comparison of Analytical Results for Decane Between ERG and Participants

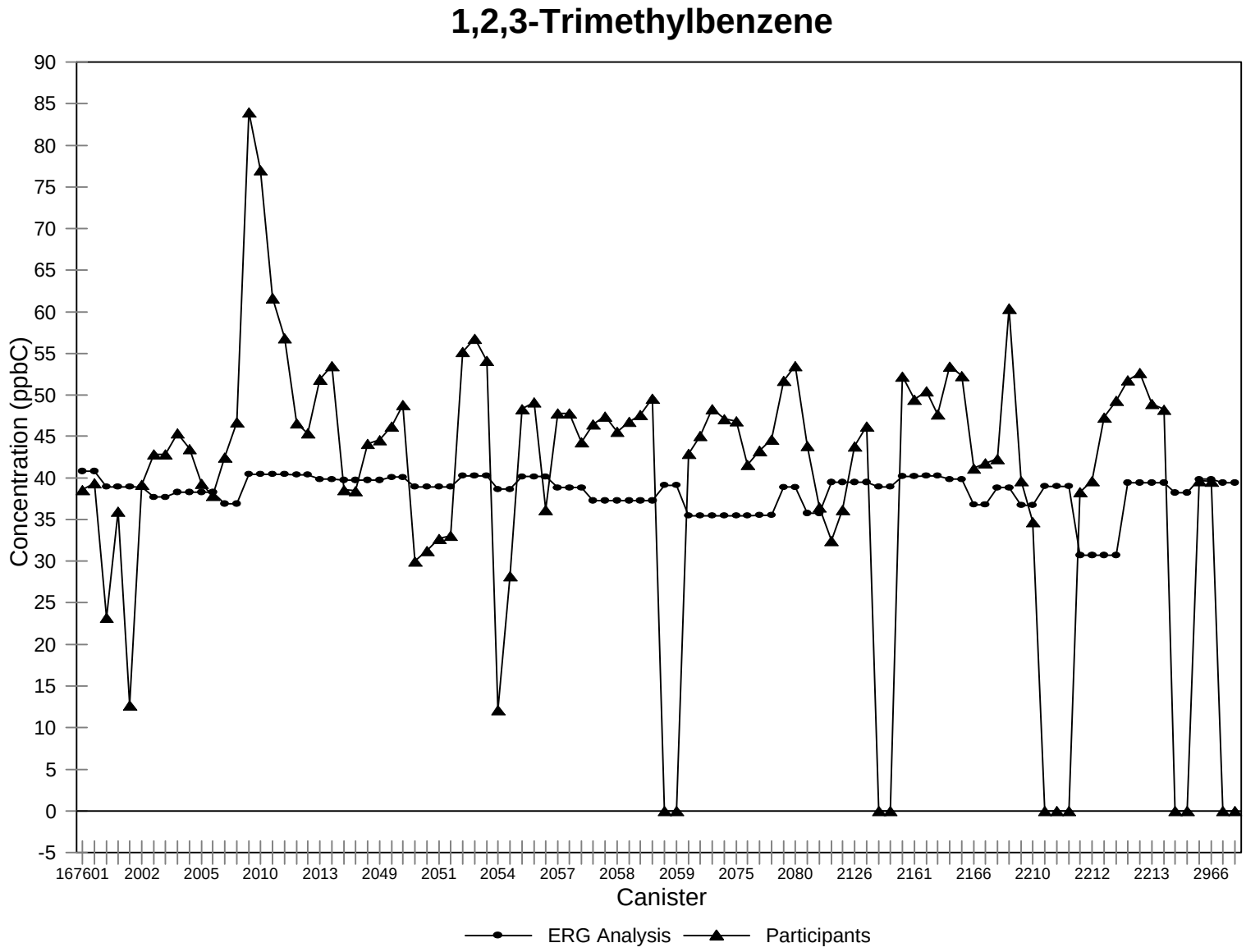

Figure 4-18. Graphical Comparison of Analytical Results for 1,2,3-Trimethylbenzene Between ERG and Participants

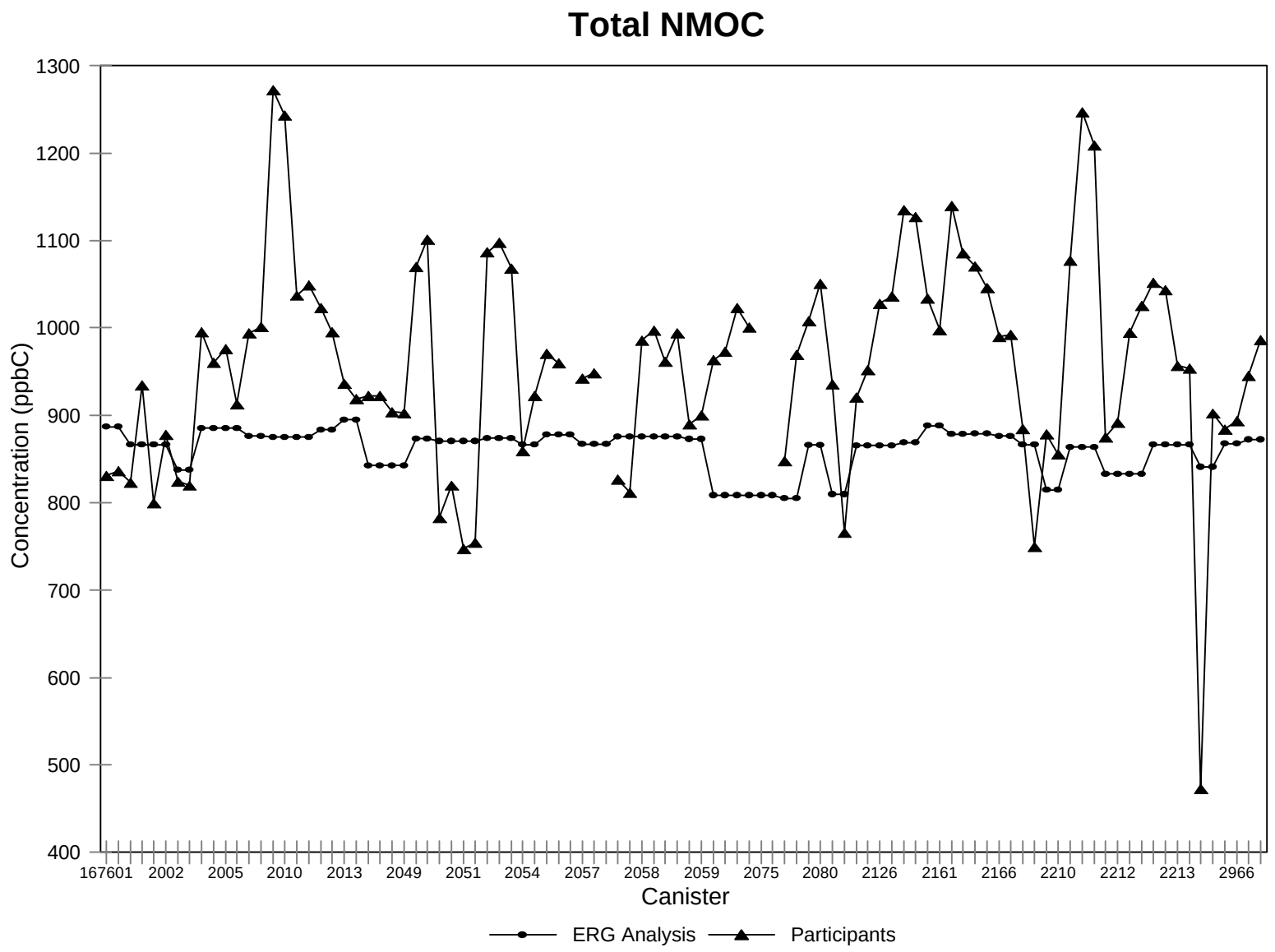

Figure 4-19. Graphical Comparison of Analytical Results for Total NMOC Between ERG and Participants

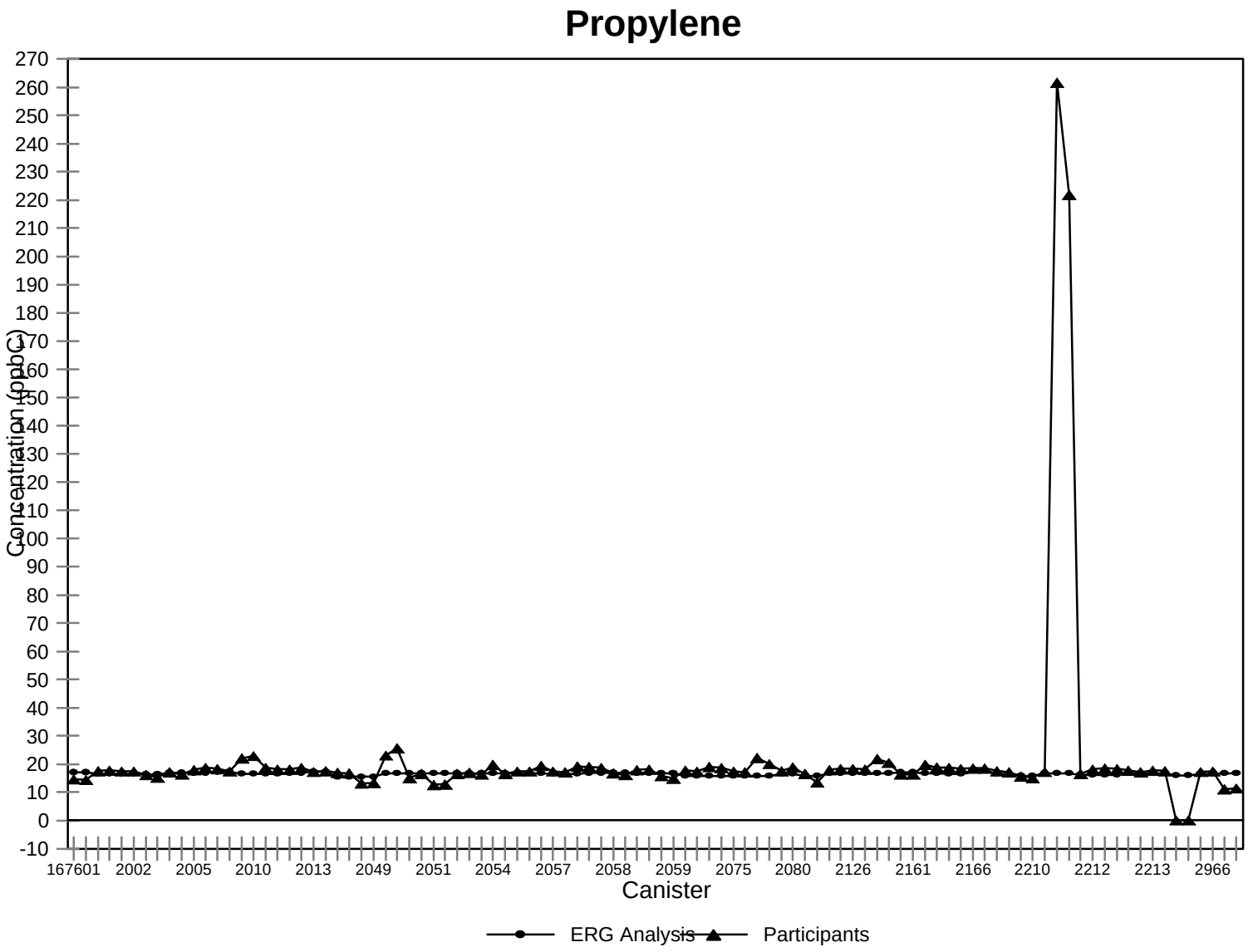

Figure 4-20. Graphical Comparison of Analytical Results for Propylene for ERG and Participants

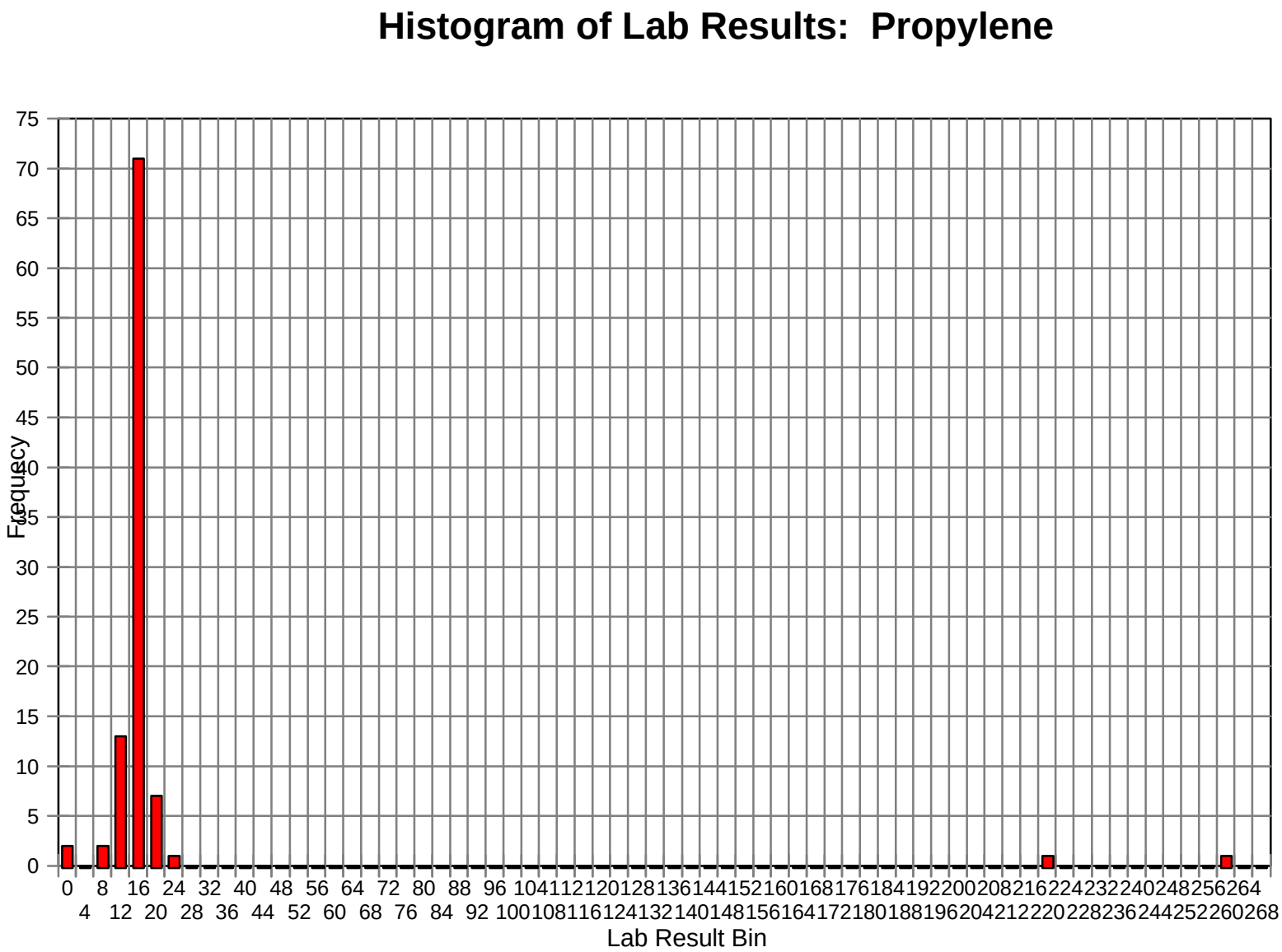

Figure 4-21. Histogram of Laboratory Results for Propylene

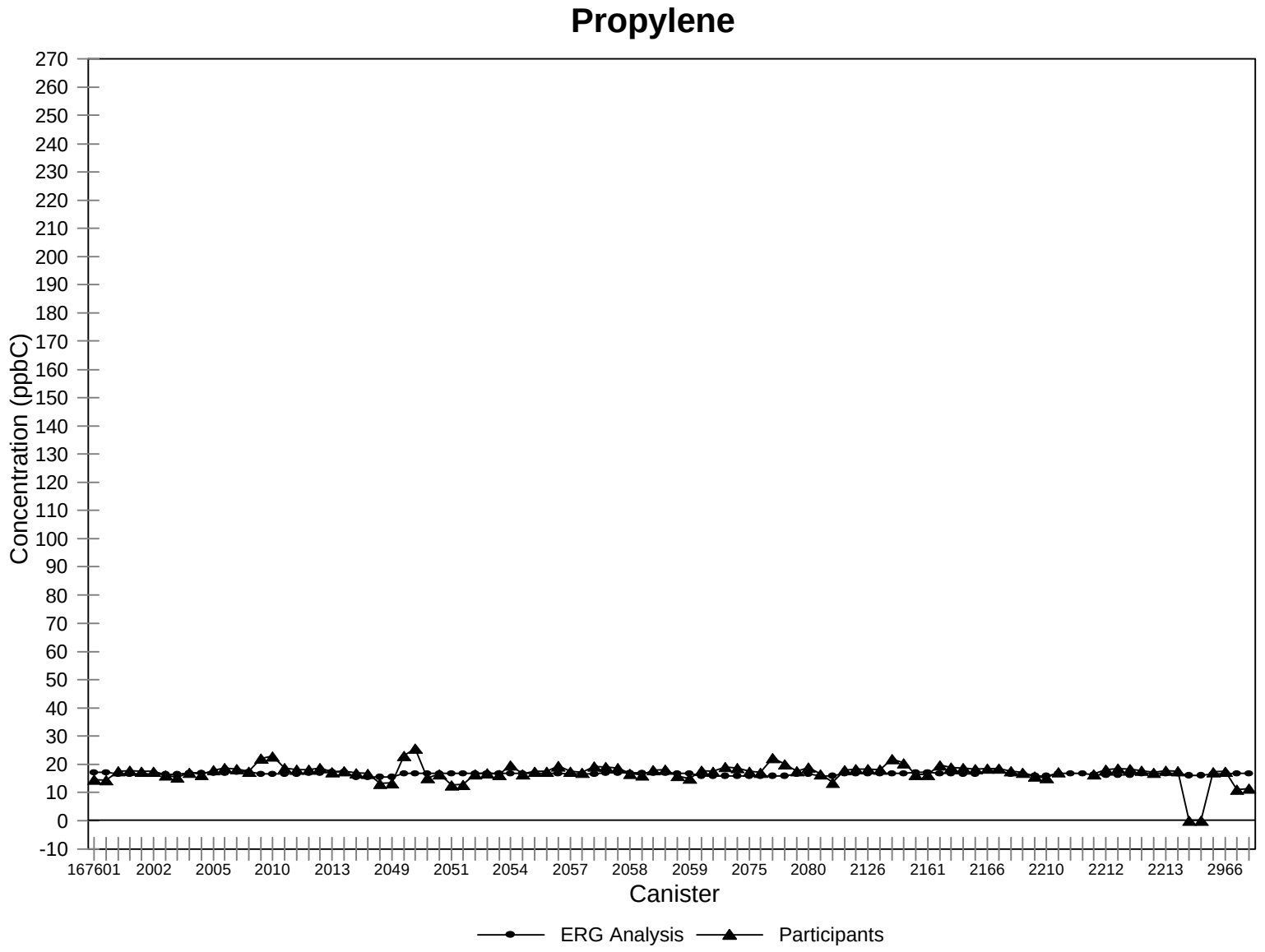

Figure 4-22. Graphical Comparison of Analytical Results for Propylene Between ERG and Participants (Outliers Excluded)

The bias of the PAMS compared to the ERG analytical results for the same canister is summarized in Figure 4-23, with the outliers for propylene excluded. Four compounds (ethylene, ethane, propane, and decane) show a negative bias; the remainder show a positive bias. If the absolute value of the bias is plotted (Figure 4-24), ethylene and ethane have the largest bias. As a group, the compounds eluting closest to propane, the standard, show the lowest bias if the outliers for propylene are excluded.

The ranges for the ERG analyses of the initial set of 40 canisters and the ranges of the analyses performed by the PAMS are shown in Table 4-5. The range was calculated as the mean ±2 standard deviations. The range of the analyses for the PAMS is larger than the range for the ERG analyses. The wider range for the PAMS can be attributed to the following factors:

- ERG analyses were all performed on the same instrument, under the same conditions and with the same calibration, in very close time proximity;
- Canisters sent to the PAMS were shipped and subjected to far more handling than the canisters in the ERG laboratory;
- PAMS used a wide range of analytical instruments and a wide range of conditions, summarized in Appendix C.
- Analyses performed by PAMS constitute 98 sets of data; ERG analyses encompass 40 canisters.

The ranges of ERG and PAMS analyses are shown graphically in Figures 4-25 through 4-27. On each of these figures, the ERG range and the PAMS range are paired within one compartment of the figure. Figure 4-25 includes the outlier data points for propylene; Figure 4-26 excludes these points.

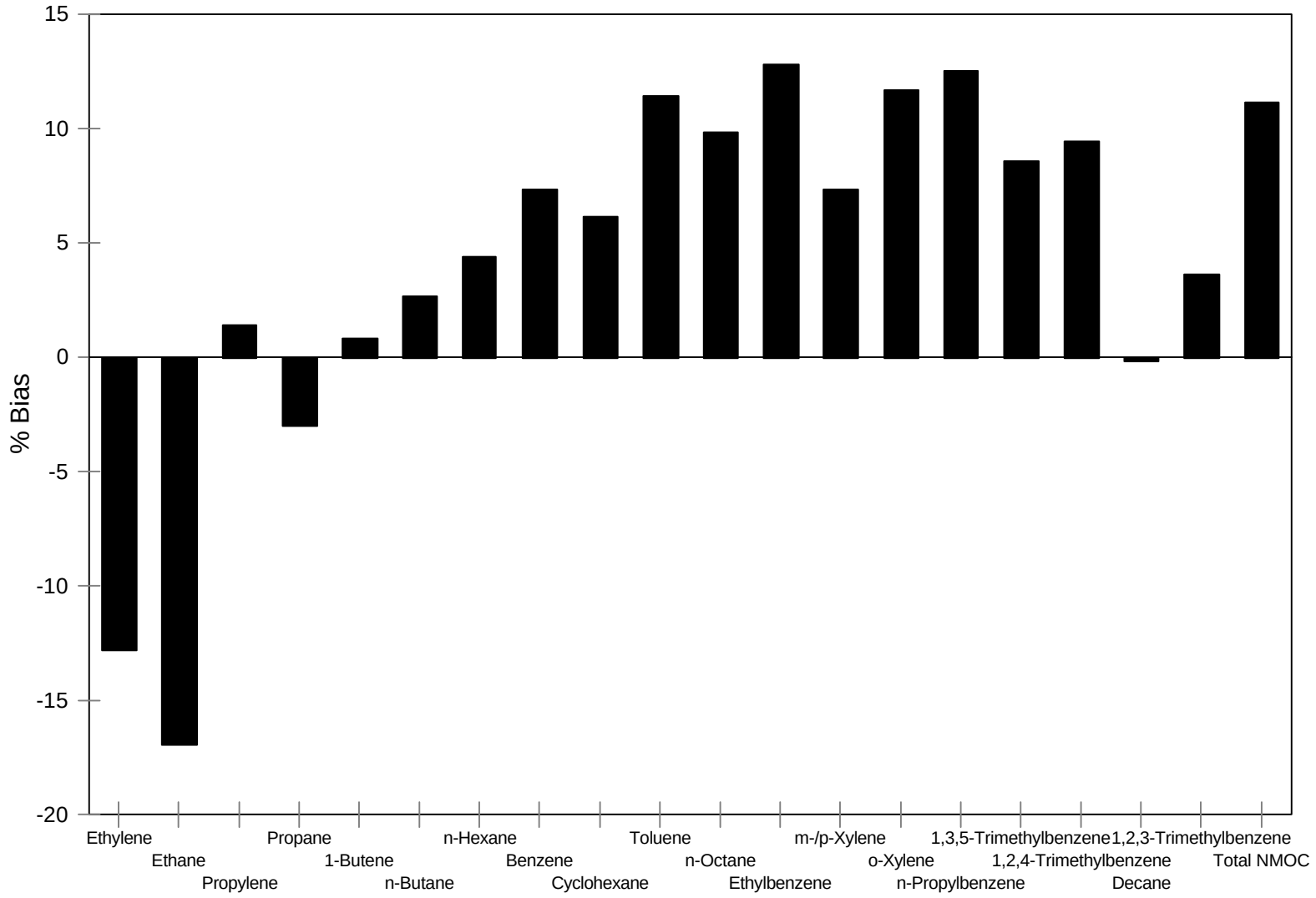

Figure 4-23. Example of the Bias of the Participants Compared to ERG Results for the One Canister

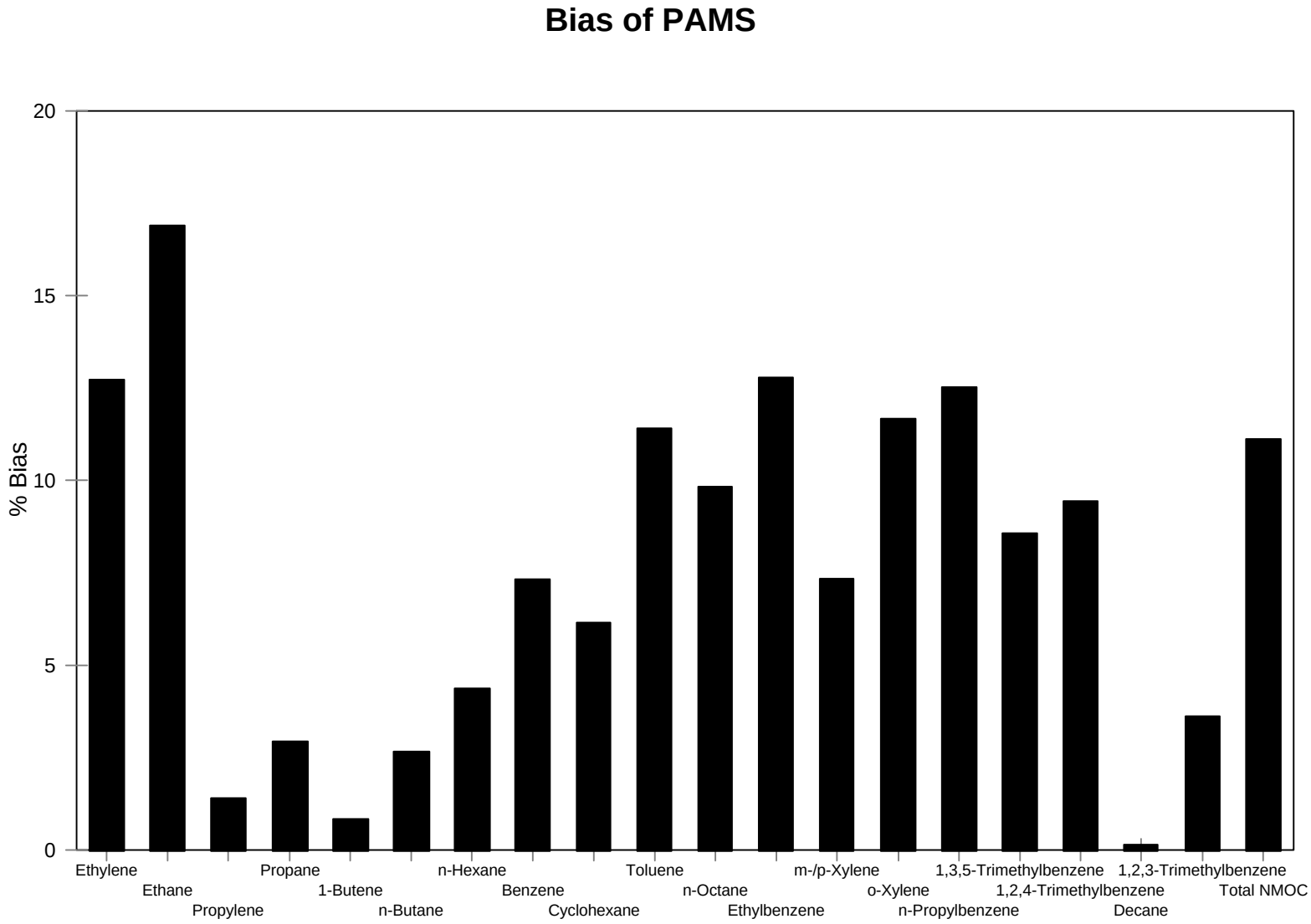

Figure 4-24. Example of the Absolute Value of the Bias for the Participants Compared to ERG Results for the One Canister

Table 4-5
Ranges for ERG Analyses and PAMS

	Range	
Compound	**ERG Analyses**	**PAMS Analyses**
ethylene	9.28 - 12.80	2.38 - 17.06
ethane	5.82 - 14.38	3.41 - 20.65
propylene	15.73 - 17.57	42.71 - 86.17
propane	20.49 - 22.61	14.41 - 27.25
1-butene	22.82 - 28.82	11.36 - 39.84
n-butane	26.35 - 29.59	21.13 - 36.13
n-hexane	37.38 - 41.82	24.72 - 57.44
benzene	66.66 - 72.94	52.16 - 97.08
cyclohexane	30.94 - 33.82	23.94 - 44.50
toluene	72.26 - 79.34	62.99 - 105.55
n-octane	46.93 - 51.73	42.13 - 65.85
ethylbenzene	78.48 - 88.64	66.90 - 121.7
m-/*p*-xylene	69.08 - 80.24	45.36 - 115.36
o-xylene	36.52 - 42.20	31.35 - 56.63
n-propylbenzene	44.17 - 55.53	31.90 - 80.82
1,3,5-trimethylbenzene	34.42 - 45.18	29.19 - 57.43
1,2,4-trimethylbenzene	32.46 - 45.06	21.31 - 63.99
n-decane	43.33 - 63.49	7.48 - 97.84
1,2,3-trimethylbenzene	30.91 - 45.43	5.62 - 73.62
Total NMOC	804.20 - 918.64	718.20 - 1198.44

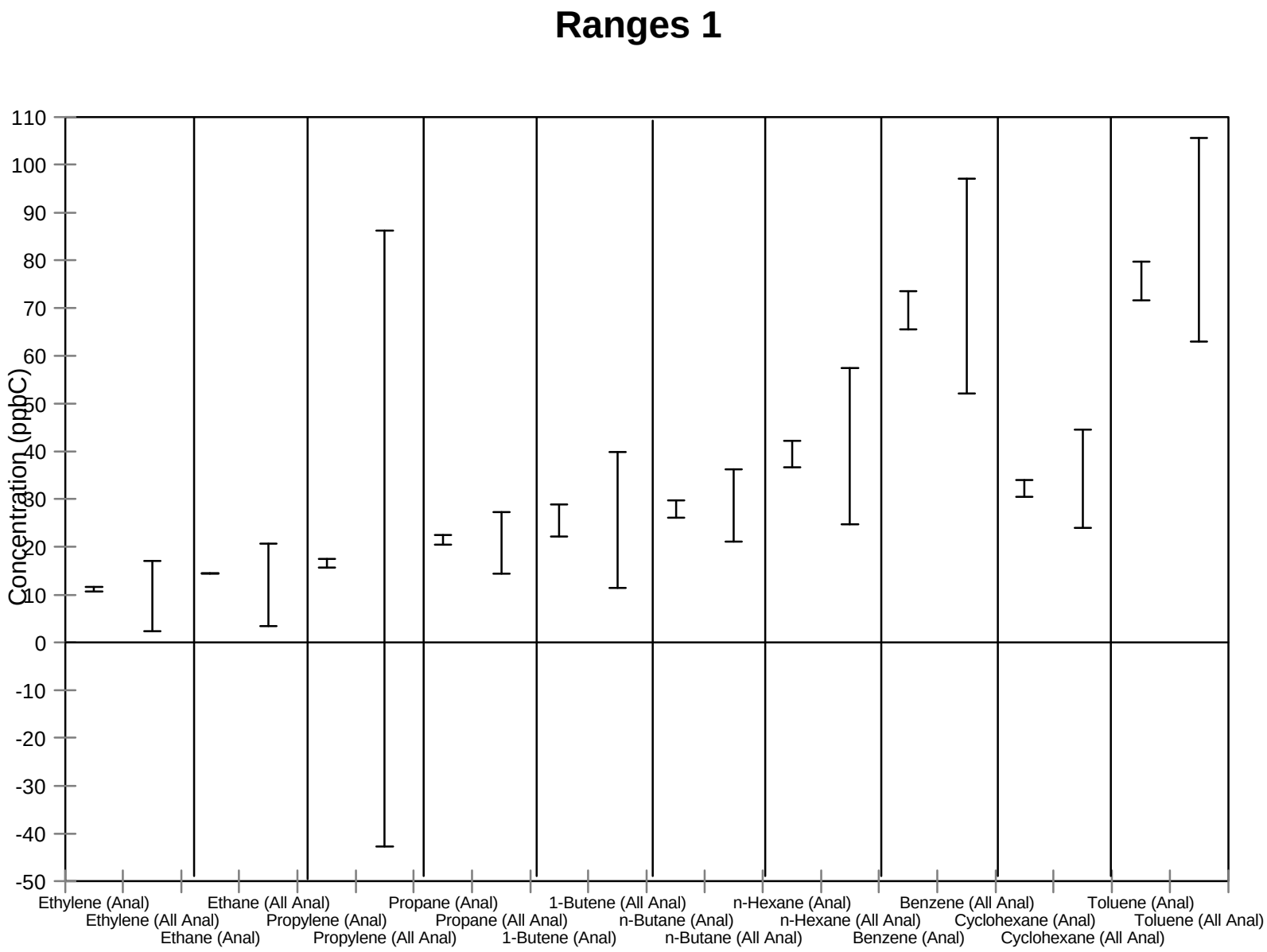

Figure 4-25. ERG Analysis Range and Participant Analysis Range, Including All Data Points (Ethylene to Toluene)

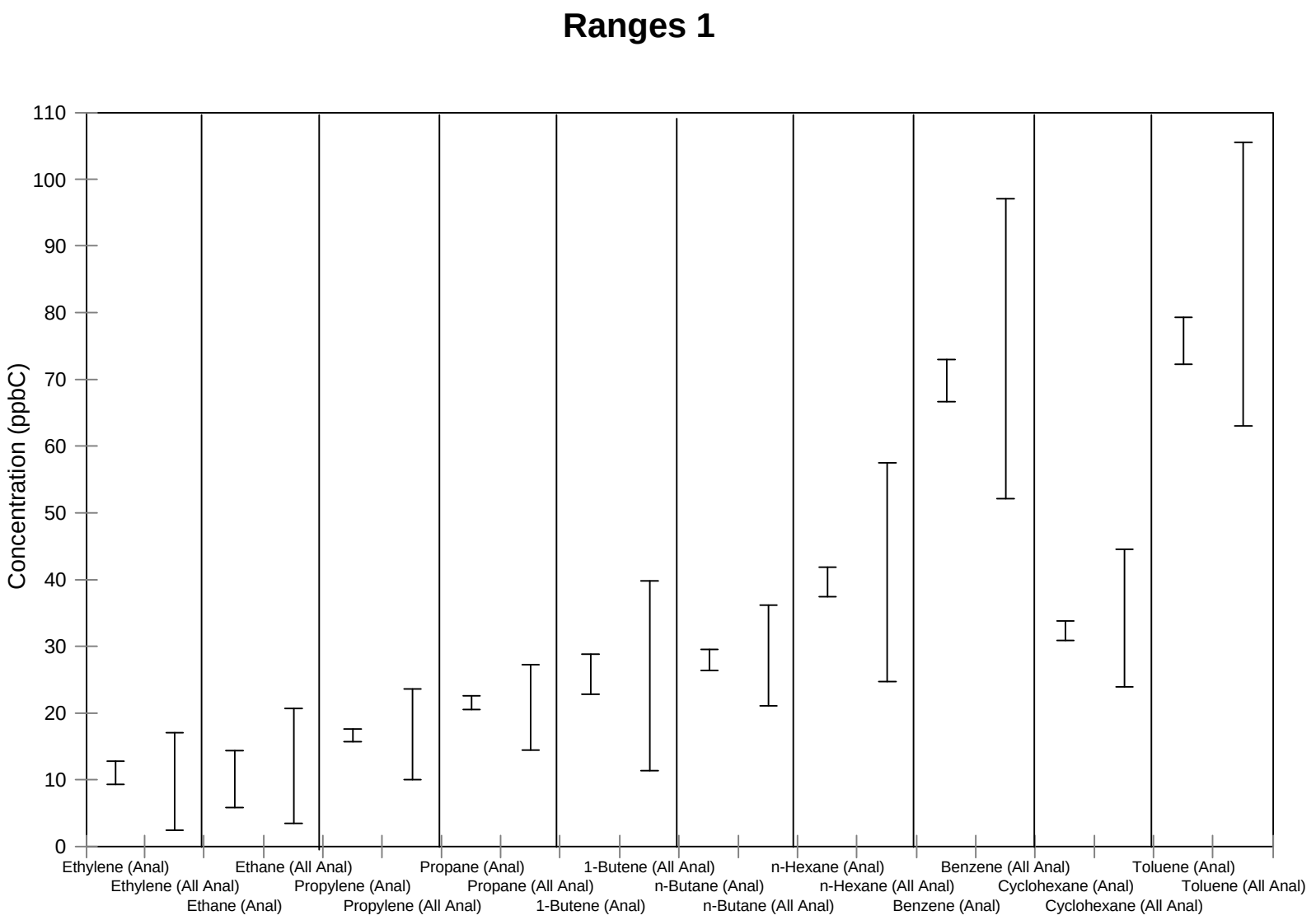

Figure 4-26. ERG Analysis Range and Participant Analysis Range, Excluding Outlier Points for Propylene (Ethylene to Toluene)

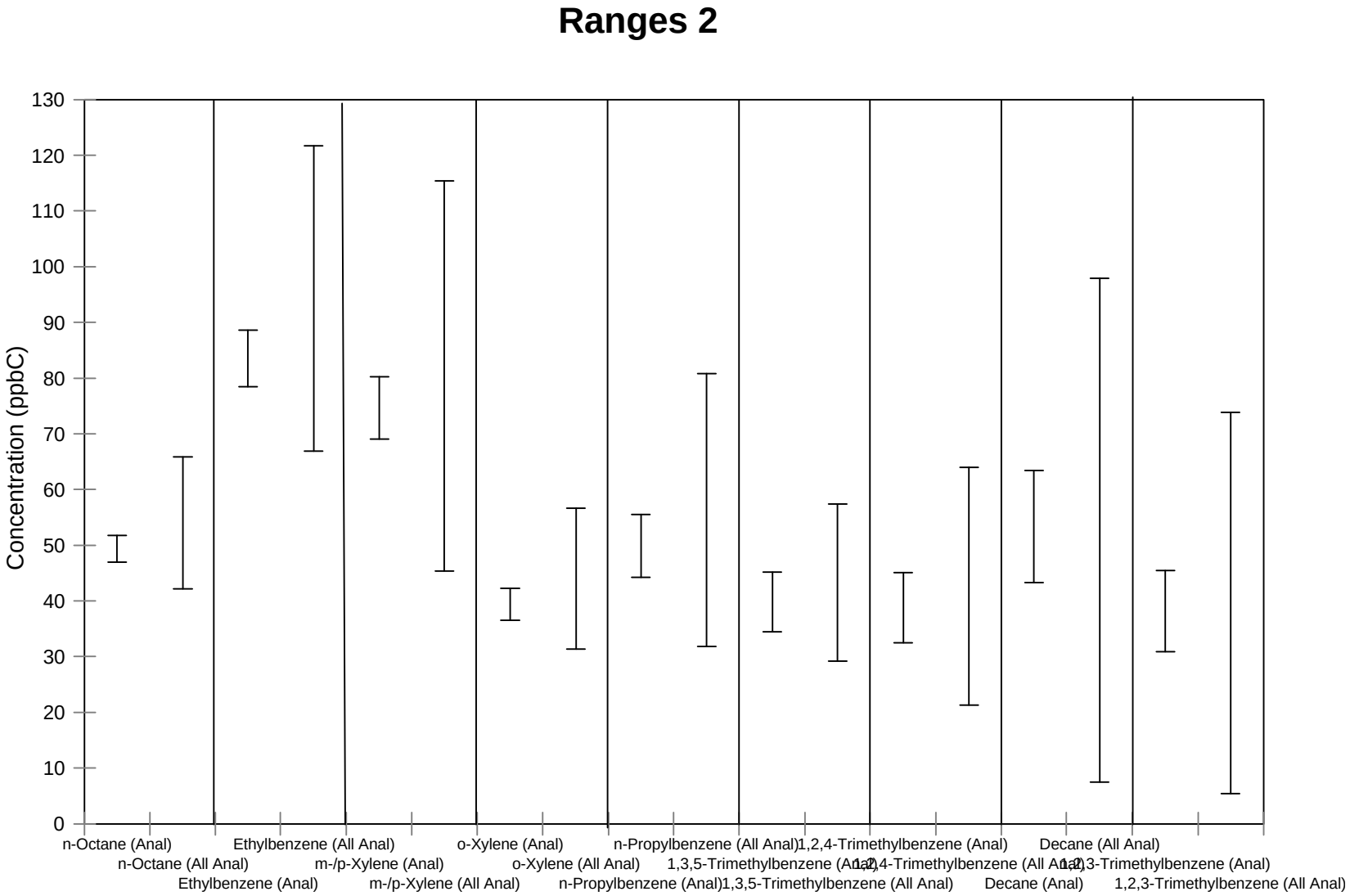

Figure 4-27. ERG Analysis Range and Participants Analysis Range (*n*-Octane to Trimethylbenzene)

A confidence interval is a range on either side of the sample mean used to estimate the population mean with a specified probability. For small sample sizes (usually less than 100), the confidence interval is calculated as follows:

$$\text{Confidence Interval} = \text{MEAN} \pm t_{(1-\alpha/2,n-1)} \times \frac{STD_s}{\sqrt{n}}$$

where:

Confidence Interval	=	the range for the estimate of the population mean for the Specified probability, 1-α (for a 95% probability level, 1-α = 0.95 and therefore α = 0.05)
$MEAN_s$	=	the sample mean
$t_{(1-\alpha/2, n-1)}$	=	the two-sided *t*-value for the specified probability (1 - α) and degrees of freedom (n-1)
STD_s	=	the sample standard deviation
n	=	the sample size

The confidence intervals for the ERG and PAMS data sets are shown graphically in Figures 4-28 through 4-30. Figure 4-28 includes the two propylene outlier points, Figure 4-29 does not include these points. Again, the ERG ranges are far narrower than the PAMS ranges, for the reasons described above.

The percent difference between replicate analyses arranged by laboratory is shown graphically in Appendix F, arranged by compound in Appendix G.

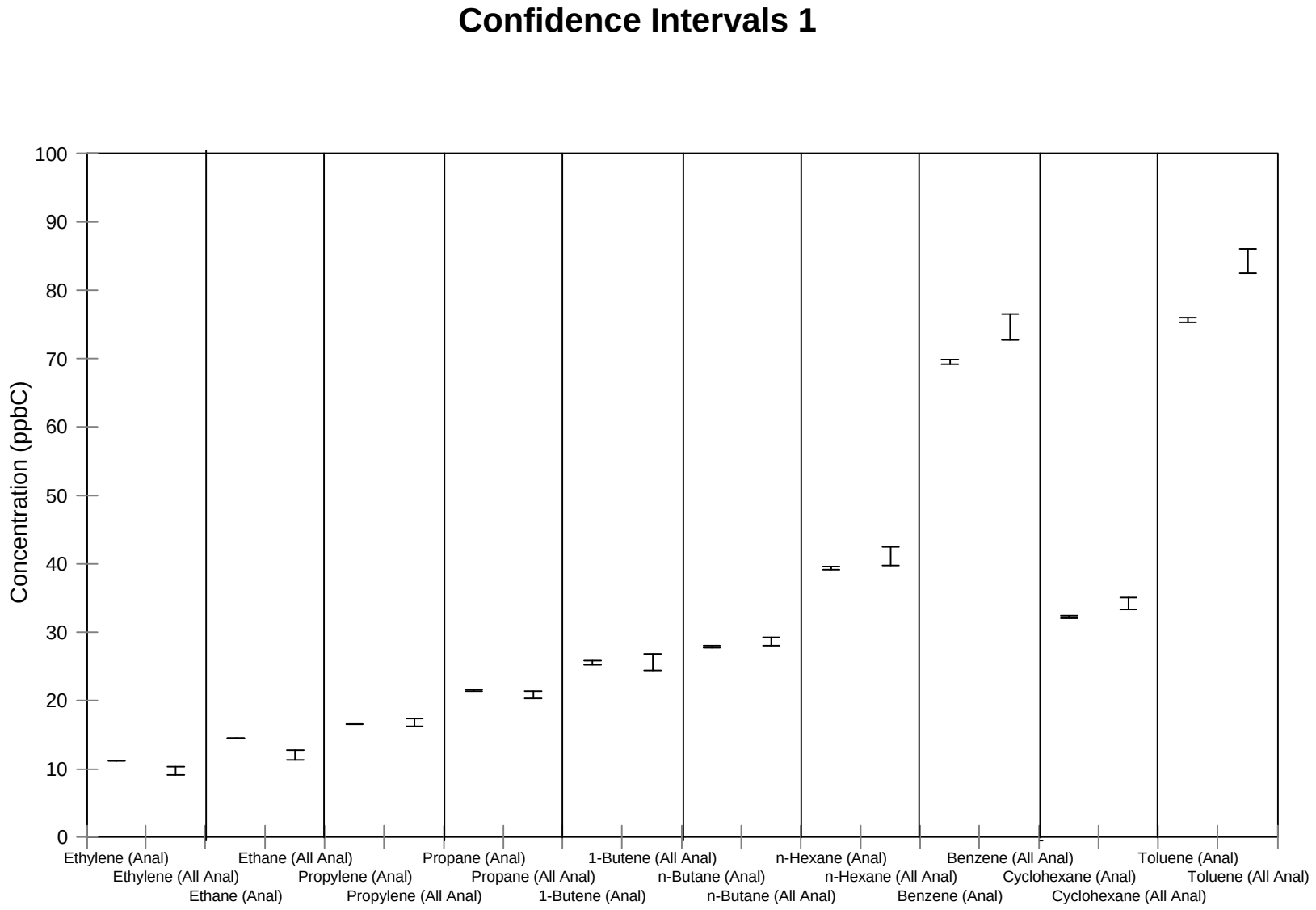

Figure 4-28. Confidence Intervals for ERG and Participant Data Sets, Including Propylene Outliers (Ethylene to Toluene)

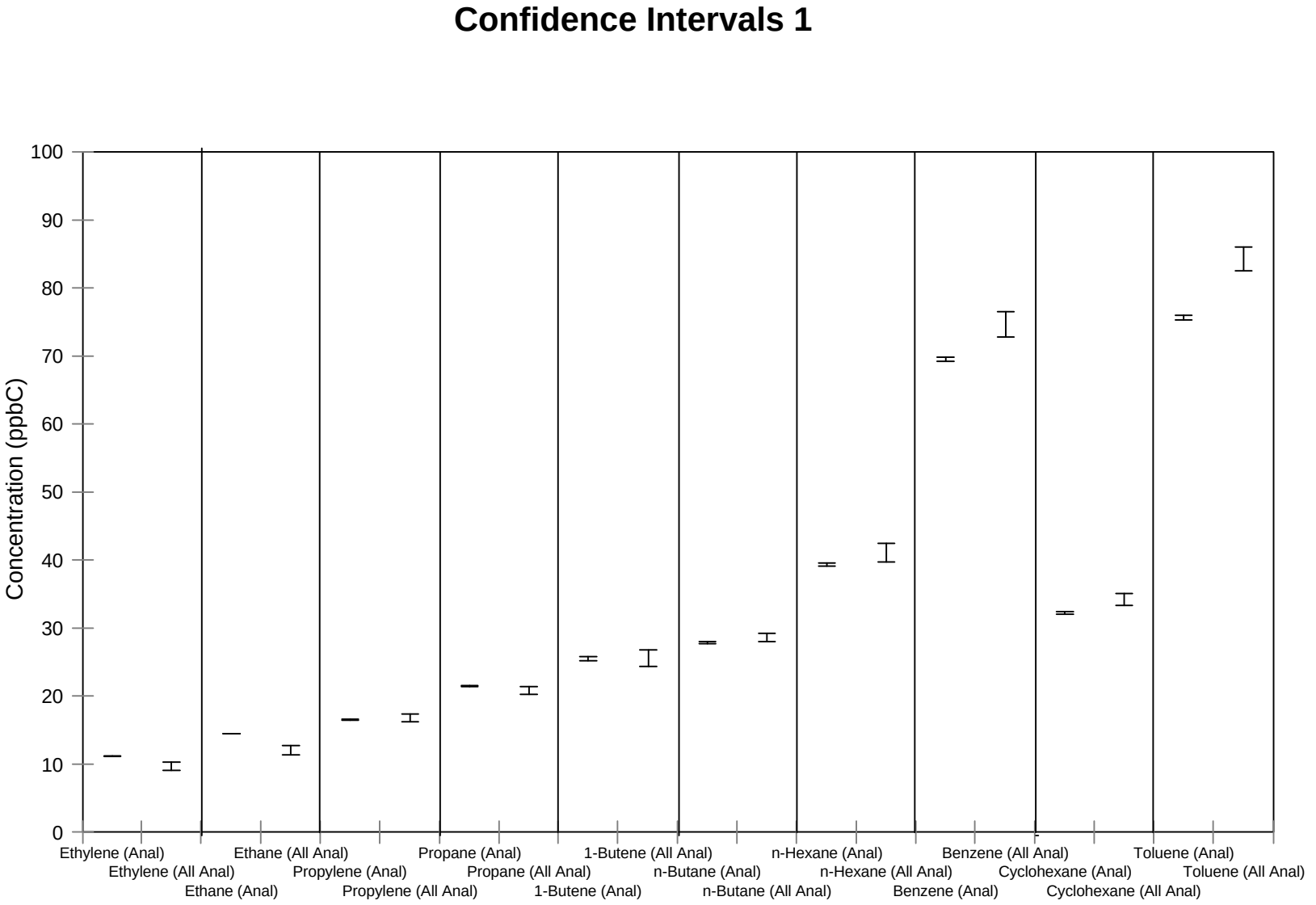

Figure 4-29. Confidence Intervals for ERG and Participant Data Sets, Excluding Propylene Outliers (Ethylene to Toluene)

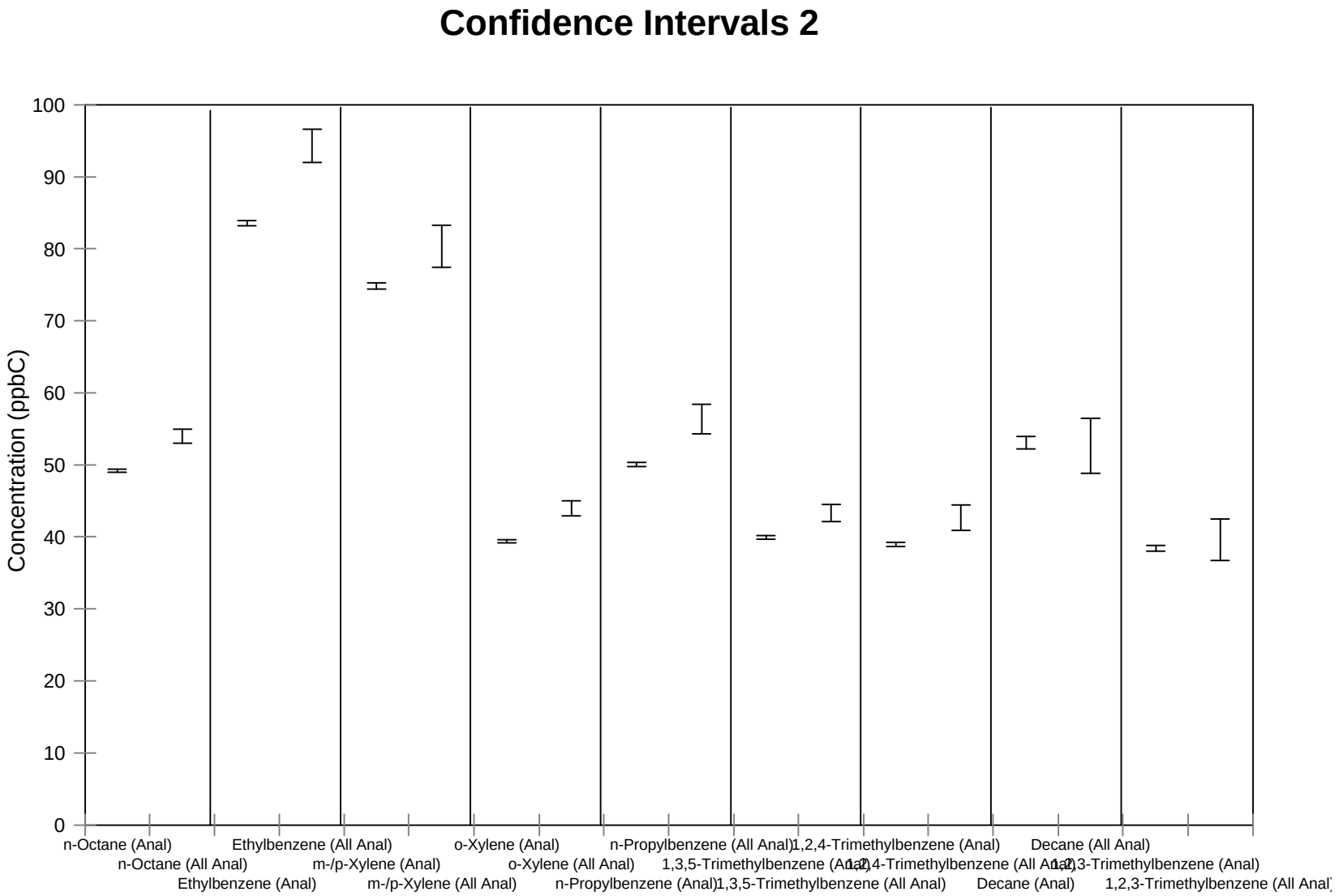

Figure 4-30. Confidence Intervals for ERG and Participant Data Sets (*n*-Octane to Trimethylbenzene)

4.2 Stability Study

Four canisters were designated at the beginning of the study as Stability Study Canisters. These canisters were filled and analyzed as part of the original batch, then set aside (not shipped to PAMS) to be re-analyzed approximately four weeks later (the actual time for the re-analysis was approximately eight weeks). Results are shown in Table 4-6 through 4-9. Figure 4-31 plots the results for the first analysis against the results for the second analysis.

If both sets of analytical results were in exact agreement (i.e., no change in canister concentration over the time period), all of the points in Figure 4-31 would fall on the 45° line. However, most points fall slightly below the 45° line. The plot indicates that results for the second analysis are slightly lower than the results for the first analysis. The calculated percent difference between the two runs ranges from -0.09 to -3.53, with the exception of ethylene and ethane. In two of the four canisters, 1-butene shows an increase, while ethylene and ethane show a decline larger than most of the other compounds. In the four canisters, the decline of ethane ranges from -15 to nearly -60% difference. Ethylene shows a slight increase (approximately 1%) in two of the canisters, and a decline of -15 to approximately -40% difference in the other two canisters. If the reason for the negative percent difference were a decline in the canister concentration of ethylene and ethane, the two compounds would be expected to decline in concentration together, in proportional amounts. This type of variation is not observed. In fact, in two of the canisters, ethylene shows a slight increase while ethane declines. At the same time, propylene, the next compound in chromatographic elution, shows a nearly constant level. The erratic measurements of ethylene and ethane may thus be due to factors associated with the analysis: possibly the sample introduction system, interaction of the compounds with the Nafion® drier, or the presence of small amounts of water in the early portion of the chromatogram. Analytical procedures for ethane and ethylene should be studied carefully for possible modification.

Table 4-6

Stability Study Performed on Canisters Retained at the ERG Laboratory Canister # 2061

Compound	1st Analysis 8/8/96	2nd Analysis 10/3/96	Precision	%Difference
ethylene	10.58	7.79	1.97	-15.19
ethane	8.18	2.63	3.92	-51.34
propylene	15.53	15.47	0.04	-0.19
propane	20.13	20.08	0.04	-0.12
1-butene	24.15	28.85	3.32	8.87
n-butane	25.68	25.38	0.21	-0.59
n-hexane	36.42	36.52	0.07	0.14
benzene	63.53	62.88	0.46	-0.51
cyclohexane	29.55	28.93	0.44	-1.06
toluene	69.21	68.63	0.41	-0.42
n-octane	45.36	45.07	0.21	-0.32
ethylbenzene	76.73	75.70	0.73	-0.68
m-/*p*-xylene	68.07	67.13	0.66	-0.70
o-xylene	37.25	35.40	1.31	-2.55
n-propylbenzene	46.47	46.71	0.17	0.26
1,3,5-trimethylbenzene	35.14	34.69	0.32	-0.64
1,2,4-trimethylbenzene	33.52	34.12	0.42	0.89
n-decane	52.35	51.61	0.52	-0.71
1,2,3-trimethylbenzene	32.61	32.90	0.21	0.44
Total NMOC	791.33	790.06	0.90	-0.08

Table 4-7

Stability Study Performed on Canisters Retained at the ERG Laboratory Canister # 2078

Compound	1st Analysis 8/8/96	2nd Analysis 10/3/96	Precision	% Difference
ethylene	10.69	10.99	0.21	1.38
ethane	8.02	5.98	1.44	-14.57
propylene	15.78	15.65	0.09	-0.41
propane	20.38	20.56	0.13	0.44
1-butene	23.62	23.53	0.06	-0.19
n-butane	26.12	25.83	0.21	-0.56
n-hexane	36.97	36.39	0.41	-0.79
benzene	64.73	63.96	0.54	-0.60
cyclohexane	30.06	29.65	0.29	-0.69
toluene	7-.47	69.51	0.68	-0.69
n-octane	46.03	45.95	0.06	-0.09
ethylbenzene	78.19	76.46	1.22	-1.12
m-/*p*-xylene	69.46	67.63	1.29	-1.33
o-xylene	36.32	35.64	0.48	-0.94
n-propylbenzene	47.22	46.35	0.62	-0.93
1,3,5-trimethylbenzene	36.01	35.19	0.58	-1.15
1,2,4-trimethylbenzene	34.61	33.94	0.47	-0.98
n-decane	52.85	51.23	1.15	-1.56
1,2,3-trimethylbenzene	33.81	32.78	0.73	-1.55
Total NMOC	802.64	793.20	6.68	-0.59

Table 4-8

Stability Study Performed on Canisters Retained at the ERG Laboratory Canister # 2208

Compound	1st Analysis 8/8/96	2nd Analysis 10/3/96	Precision	% Difference
ethylene	10.62	4.86	4.07	-37.21
ethane	9.03	2.40	4.69	-58.01
propylene	15.57	15.40	0.12	-0.55
propane	19.97	20.02	0.0-4	0.13
1-butene	23.38	27.62	3.00	8.31
n-butane	25.68	25.30	0.27	-0.75
n-hexane	36.03	36.43	0.28	0.55
benzene	63.70	62.36	0.95	-1.06
cyclohexane	29.56	28.90	0.47	-1.13
toluene	69.60	68.03	1.11	-1.14
n-octane	45.94	44.52	1.00	-1.57
ethylbenzene	77.32	74.47	2.02	-1.88
m-/*p*-xylene	68.85	66.08	1.96	-2.05
o-xylene	36.00	34.90	0.78	-1.55
n-propylbenzene	46.91	44.85	1.46	-2.24
1,3,5-trimethylbenzene	36.37	34.31	1.46	-2.91
1,2,4-trimethylbenzene	35.28	33.46	1.29	-2.65
n-decane	52.44	49.06	2.39	-3.33
1,2,3-trimethylbenzene	34.91	32.53	1.68	-3.53
Total NMOC	795.73	768.22	19.45	-1.76

Table 4-9

Stability Study Performed on Canisters Retained at the ERG Laboratory Canister # GP00036

Compound	1st Analysis 8/8/96	2nd Analysis 10/3/96	Precision	% Difference
ethylene	10.70	20.93	0.16	1.06
ethane	11.89	6.16	4.05	-31.75
propylene	15.77	15.53	0.17	-0.77
propane	20.42	20.58	0.11	0.39
1-butene	26.97	24.12	2.02	-5.58
n-butane	26.09	25.83	0.18	-0.50
n-hexane	36.93	36.24	0.49	-0.94
benzene	64.11	63.47	0.45	-0.50
cyclohexane	29.83	29.47	0.25	-0.61
toluene	68.99	68.82	0.12	-0.12
n-octane	46.79	46.16	0.45	-0.68
ethylbenzene	75.15	74.87	0.20	-0.19
m-/*p*-xylene	65.66	65.42	0.17	-0.18
o-xylene	34.41	34.33	0.06	-0.12
n-propylbenzene	45.50	45.55	0.04	0.05
1,3,5-trimethylbenzene	32.40	32.31	0.06	-0.14
1,2,4-trimethylbenzene	29.86	30.31	0.32	0.75
n-decane	51.51	51.26	0.18	-0.24
1,2,3-trimethylbenzene	28.37	28.61	0.17	0.42
Total NMOC	782.13	776.89	3.71	-0.34

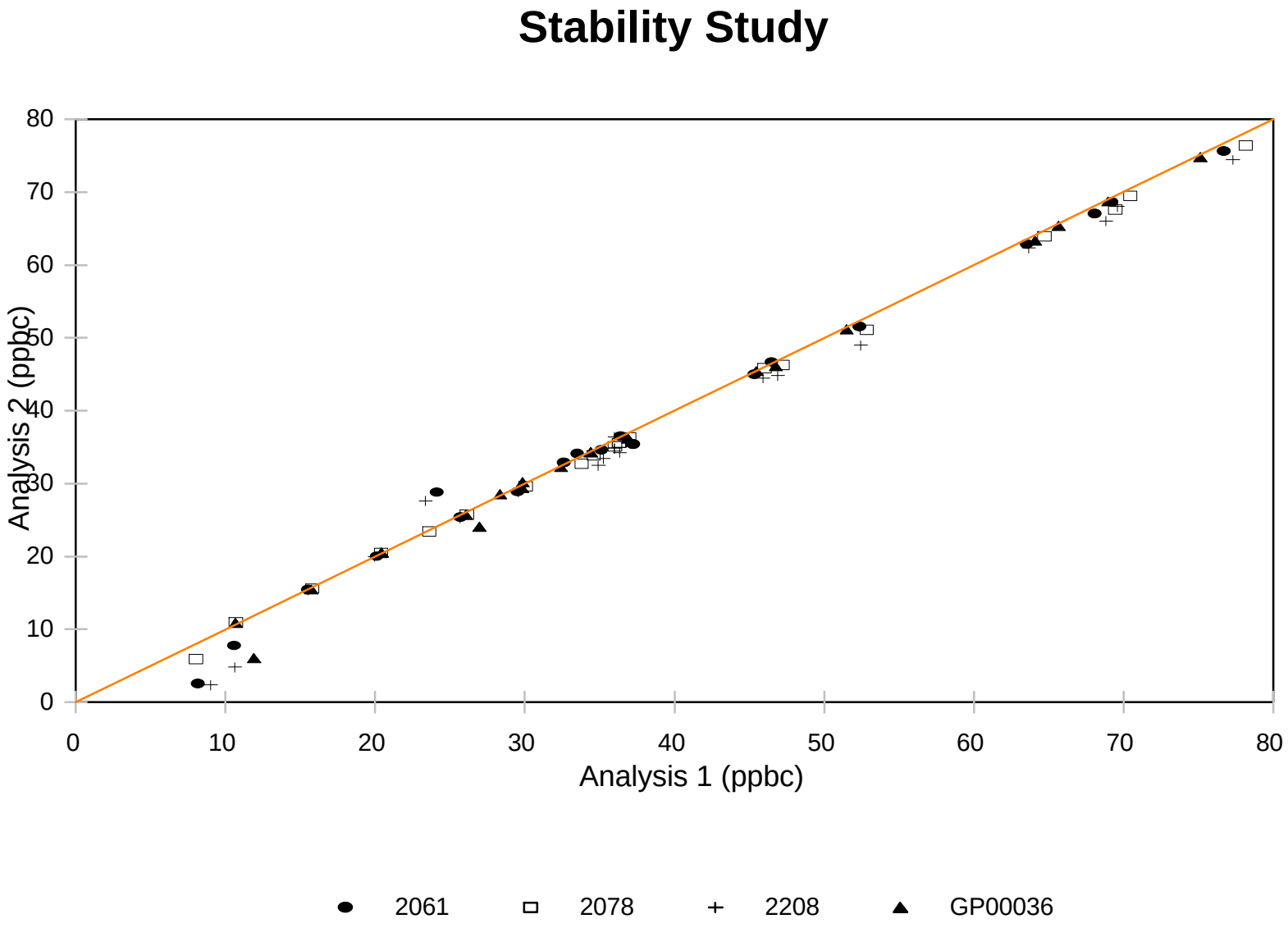

Figure 4-31. Stability Study for Canisters Retained at the ERG Laboratory

4.3 Outlier Analysis

An outlier analysis was conducted for each compound using all nonzero values from all PAMS sites for both Analysis 1 and Analysis 2. Any outlier analysis contains subjective elements, but the philosophy used in this outlier analysis was very conservative--only the most blatantly obvious of the candidate outliers were labeled as such.

Candidate outliers were identified by examing the data distribution for gaps between the main body of data and extreme values on either end of the distribution. Two methods, the NSI method and the F-spread method, were used to determine cutoff points, beyond which, data points would be considered as candidate outliers for further scrutiny.

In the NSI method, the data distribution was classified as normal, lognormal, or other (not normal or lognormal), using the SAS UNIVARIATE procedure. Candidate outliers were identified according the data distribution classification, in the following sequence:

- *Normal Distribution:* any data point a distance of more than 3 times the standard deviation from the mean
- *Lognormal Distribution (but not Normal):* any data point a distance of more than 3 times the standard deviation from the mean of the natural logarithms
- *Other Distribution (not Normal or Lognormal):* any data point a distance of more than 6 times the standard deviation from the mean

In the F-spread method, the F-spread was calculated as the difference between the 75th and 25th percentiles. Any data point a distance of more than 1.5 times the F-spread from the mean was identified as a candidate outlier.

When the candidate outliers were identified from the NSI and F-spread methods, they were visually identified on a plot of the data distribution. If there was a substantial gap between the main body of data and the candidate outlier(s), if no other data points were located in this region of the data distribution, and the value of the candidate outlier(s) was substantially different from the other data points, the candidate outlier(s) was officially classified as an outlier(s).

Only two points, both for replicate determinations of propylene from the same PAMS site and canister, were officially classified as outliers.

4.4 Additional Compounds Identified

In addition to the ozone precursors spiked into the performance evaluation canisters, four additional compounds were spiked: 1,3-butadiene, *tert*-butyl methyl ether, 1-hexene, and 1,1,1-trichloroethane. All of these additional compounds could be observed in the PAMS analysis, with the exception of *tert*-butyl methyl ether which would have been removed if the analytical system used in the analysis was equipped with a drier. *tert*-Butyl methyl ether, 1-hexane, and 1,1,1-trichloroethane were reported in only four analyses; 1,3-butadiene was reported in only eight analyses.

The introduction of the additional compounds provided a challenge to the compound identification procedures at a number of PAMS. Many PAMS reported additional compounds that were not spiked into the canisters. Some laboratories carefully characterized the slightest peak observed above the chromatographic baseline. The additional compounds reported and the number of times they were reported are shown in Table 4-10. The most frequently identified additional compound, 2-methyl-1-pentene, was not spiked into the canisters. One of the additional spiked compounds, 1-hexene, was frequently misidentified as 2-methyl-1-pentene. However, ten analyses reported 2,3-dimethylbutane (not present) and six analyses reported 2-methylpentane, both misidentifications of *tert*-butyl methyl ether. Five analyses reported 2,4-dimethylpentane, a misidentification of 1,1,1-trichloroethane.

More than twenty analysis reports each identified isopropylbenzene, *m*-ethyltoluene, *o*-ethyltoluene, *m*-diethylbenzene, and *n*-undecane, none of which were components of the

Table 4-10

Additional Compounds Reported and Frequency of Reporting

Compound	Frequency	Compound	Frequency
acetylene	2	2,4-dimethylpentane	5
isobutane	15	1,1,1-trichloroethane	4
1,3-butadiene	8	2-methylhexane	1
trans-2-butene	24	3-methylhexane	5
cis-2-Butene	18	2,2,4-trimethylpentane	2
isopentane	4	*n*-heptane	5
1-pentene	7	methylcyclohexane	2
n-pentane	2	3-methylheptane	28
isoprene	5	styrene	26
*t*rans-2-pentene	1	*n*-nonane	9
cis-2-pentene	1	isopropylbenzene	43
2,2-dimethylbutane	2	*m*-ethyltoluene	22
cyclopentane	1	*p*-ethyltoluene	7
2,3-dimethylbutane	10	*m*-/*p*-ethyltoluene	2
3-methylpentane	6	*o*-ethyltoluene	27
methyl *t*-butyl ether	4	*m*-diethylbenzene	39
3-methylpentane	4	*p*-diethylbenzene	16
1-hexene	4	*m*-/*p*-diethylbenzene	2
2-methyl-1-pentene	54	*n*-undecane	21
methylcyclopentane	8	unknown (one or more)	22

gaseous mixture spiked into the canisters. Because of the frequency of the reports of the occurrence of these compounds, ERG exhaustively characterized the four stability study canisters retained in the ERG laboratory. From the examination of this limited sample (Table 4-11), ERG concludes that several of these compounds are indeed present in the canisters at trace levels (< l ppbC). It is not known whether these compounds are present as a residual from previous samples that were not completely removed in the canister cleaning process, as an impurity in the cylinder gases used to prepare the performance evaluation standards, or as a residual in the analytical system. Blank canister samples (humidified zero air) prepared and analyzed in the ERG laboratory do not show the presence of these three- and four-carbon alkylbenzenes or undecane at concentrations at or above the method detection limit.

Table 4-11
Additional Compounds Identified in ERG Stability Study Canisters

Additional Compounds	Frequency (Out of Four Canisters)
trans-2-butene	2
cis-2-butene	2
isopentane	1
2-methylpentane	2
trans-2-hexene	1
cis-2-hexene	2
3-methylhexane	1
3-methylheptane	1
m-diethylbenzene	2
p-diethylbenzene	4

4.5 ERG Re-Analysis of Performance Evaluation Canisters

As an additional feature of the Performance Evaluation program, sixteen of the canisters returned from the PAMS were re-analyzed by ERG upon their return. The results for the original ERG analysis, the second ERG analysis, the percent difference between the two ERG analyses, as well as the results of the PAMS analyses for each canister are shown in Appendix D. A general criterion for selection of a particular canister for re-analysis was a significant difference between the PAMS results and the ERG original analysis results (the repeated ERG analysis always reinforced the first ERG analysis results). For example, the canister that showed the outlier points for the propylene analysis was re-analyzed upon its return to ERG. The repeated analysis by ERG showed a percent difference of approximately -4% from the original analysis. The values for percent difference (equation below) for the ERG re-analysis are summarized for each analyte in Table 4-12.

$$\% \text{ Difference} = \frac{ERG_2 - ERG_1}{ERG_1} \times 100$$

where:

ERG_1 = first ERG analysis

ERG_2 = second ERG analysis

There are some isolated spikes in the values of the differences, but the results are generally negative and approximately 10% lower than the original analysis. The widest ranges are shown by propylene, 1-butene, *n*-butane, and benzene. It is interesting to note that the range of differences for the ERG TNMOC analyses is no wider than most of the individual analytes.

The repeated analysis of these canisters was performed at the same time as the repeated analysis of the stability study canisters retained by ERG. However, the drop in compound

Table 4-12

Percent Difference Between First and Second ERG Analysis

Ethylene	Ethane	Propylene	Propane	1-Butene
-10.41	-10.07	-11.18	-9.99	-9.28
-10.82	-8.43	-19.07	-10.56	-9.89
-10.28	-7.36	-15.75	-10.08	-11.23
-11.44	-8.64	-9.13	-10.77	-4.98
-10.06	-7.35	-26.07	-9.78	-5.83
-10.23	-8.49	-0.28	-10.14	30.03
-10.85	-9.58	36.54	-10.49	-7.54
0.28	-0.46	1.08	-0.94	3.43
-10.86	-7.63	-44.89	-10.13	-9.73
-10.97	-8.34	-19.17	-10.56	-11.64
-9.75	-12.49	-15.50	-9.66	3.78
-9.91	-8.75	49.21	-9.57	-7.09
-1.17	1.09	14.80	-1.20	-2.75
-10.16	-8.68	-4.06	-9.70	-3.95
-10.29	-7.27	-6.23	-9.75	-7.68
-5.56	-4.39	3.90	-5.40	-5.97
Mean: -8.91	-7.31	-4.11	-8.67	-3.77
SD: 3.57	3.42	22.95	3.21	10.08
%CV: -39.95	-46.83	-558.02	-37.00	-267.40

Table 4-12
Continued

n-Butane	*n*-Hexane	Benzene	Cyclohexane	Toluene
-29.23	-9.55	-4.14	-8.64	-10.76
0.65	-10.48	-1.82	-10.95	-11.10
13.10	-10.96	-3.61	-9.40	-10.45
10.79	-12.26	-3.62	-10.85	-11.57
-7.71	-8.63	-2.01	-9.35	-10.14
-6.72	-6.51	-1.08	-9.53	-7.68
7.41	-9.39	-3.47	-11.74	-10.69
8.68	-0.22	3.47	0.44	-0.97
16.70	-9.83	-5.03	-11.63	-10.18
-9.48	-10.27	-4.02	-11.32	-11.01
-16.80	-8.28	-3.63	-9.09	-9.49
8.02	-8.22	-3.03	-8.99	-10.25
-3.01	-2.59	3.43	0.16	-2.98
1.54	-9.45	-2.44	-9.57	-10.18
0.52	-9.55	-3.69	-9.51	-10.29
-57.37	-4.78	1.90	-6.07	-6.25
Mean: -3.93	-8.19	-2.04	-8.50	-9.00
SD: 18.53	3.19	4.57	3.71	3.06
%CV: -471.20	-38.99	-222.84	-43.58	-34.03

Table 4-12
Continued

n-octane	ethylbenzene	*m*-/*p*-xylene	*o*-xylene	*n*-propylbenzene
-8.74	-9.92	-9.30	-9.59	-9.23
-6.28	-11.27	-8.37	-10.71	-11.75
-6.46	-12.87	-8.83	-9.95	-11.25
-5.81	-14.01	-7.81	-11.63	-14.65
-6.17	-8.35	-7.61	-9.19	-6.67
-6.40	0.72	-7.43	-8.04	-4.42
-5.96	-9.29	-8.28	-9.91	-9.06
1.55	1.64	-0.01	0.33	2.14
-6.08	-10.31	-9.78	-10.12	-9.81
-7.07	-11.07	-9.69	-10.59	-10.80
-7.34	-6.99	-8.76	-8.25	-6.82
-6.10	-8.69	-8.46	-9.46	-6.34
0.60	-2.54	-0.28	-1.26	-3.29
-6.07	-9.28	-7.68	-10.27	-8.65
-6.47	-9.61	-8.88	-9.70	-8.58
-2.47	-5.40	-3.53	-4.80	-6.60
Mean: -5.23	-7.95	-7.16	-8.32	-7.86
SD: 2.79	4.49	3.09	3.43	3.91
%CV: -52.41	-56.42	-43.09	-41.25	-49.67

Table 4-12
Continued

1,3,5-trimethylbenzene	1,2,4-trimethylbenzene	*n*-decane	1,2,3-trimethylbenzene	Total NMOC
-9.40	-10.47	-9.68	-9.93	-8.62
-10.80	-11.18	-10.64	-11.05	-9.14
-11.07	-10.55	-12.24	-10.03	-8.86
-13.83	-13.40	-12.66	-12.59	-9.76
-6.75	-8.55	-8.54	-9.03	-7.31
-1.11	-4.49	-4.41	-7.17	-6.88
-8.33	-9.69	-9.21	-9.48	-8.58
8.96	0.73	-0.03	1.19	2.90
-9.52	-10.24	-9.92	-9.87	-9.04
-10.14	-10.72	-10.25	-10.38	-9.30
-6.26	-7.99	-9.17	-7.88	-7.18
-7.23	-7.80	-6.89	-9.57	-7.08
-2.44	-2.88	-3.22	-2.10	-0.25
-8.39	-9.35	-9.61	-9.85	-7.97
-8.45	-9.61	-9.71	-9.80	-8.23
-5.60	-5.90	-5.04	-5.37	-4.59
Mean: -6.90	-8.26	-8.20	-8.30	-6.86
SD: 5.28	3.56	3.42	3.51	3.48
%CV: -76.53	-43.11	-41.70	-42.29	-50.71

concentrations for the canisters returned from the external laboratories is considerably larger because:

- These canisters have been shipped twice and losses could have occurred in shipping and handling.
- The canisters have been opened at least four times for analyses (at least twice by the PAMS and twice by ERG).

Even under these conditions of shipping and handling for these canisters, the concentration of most of the analytes declined 10% or less.

The comparison of ERG results for the first and second analyses of the four canisters retained at the ERG laboratory and the sixteen canisters shipped to PAMS sites and returned is shown graphically by compound in Figures 4-32 through 4-51. If ERG Analysis 1 has the same result as ERG Analysis 2, the point falls on the line drawn at a 45-degree angle in the plot. A point above the line indicates that Analysis 2 had a higher result than Analysis 1, while points below the line show that Analysis 2 had a lower result than Analysis 1.

4.6 Additional Statistical Calculations Relative to the Mean of the PAMS Analyses Excluding Outliers

The statistical calculations discussed in the previous sections have compared analytical results obtained by the PAMS sites to the analytical results obtained by ERG in the ERG laboratories. Additional statistical calculations were performed comparing the analytical results obtained by the PAMS sites to the mean of the results obtained by the PAMS sites, excluding outliers. As discussed in Section 4.3, only two data points were removed from the dataset as outliers according to the statistical evaluation. Values for compounds not reported were not included in the statistical calculations: i.e., if ten determinations did not report 1,2,3-trimethylbenzene, the number of data points used in the statistical calculations was 88 rather than 98. The compounds most frequently not reported by the PAMS sites are shown in Table 4-13.

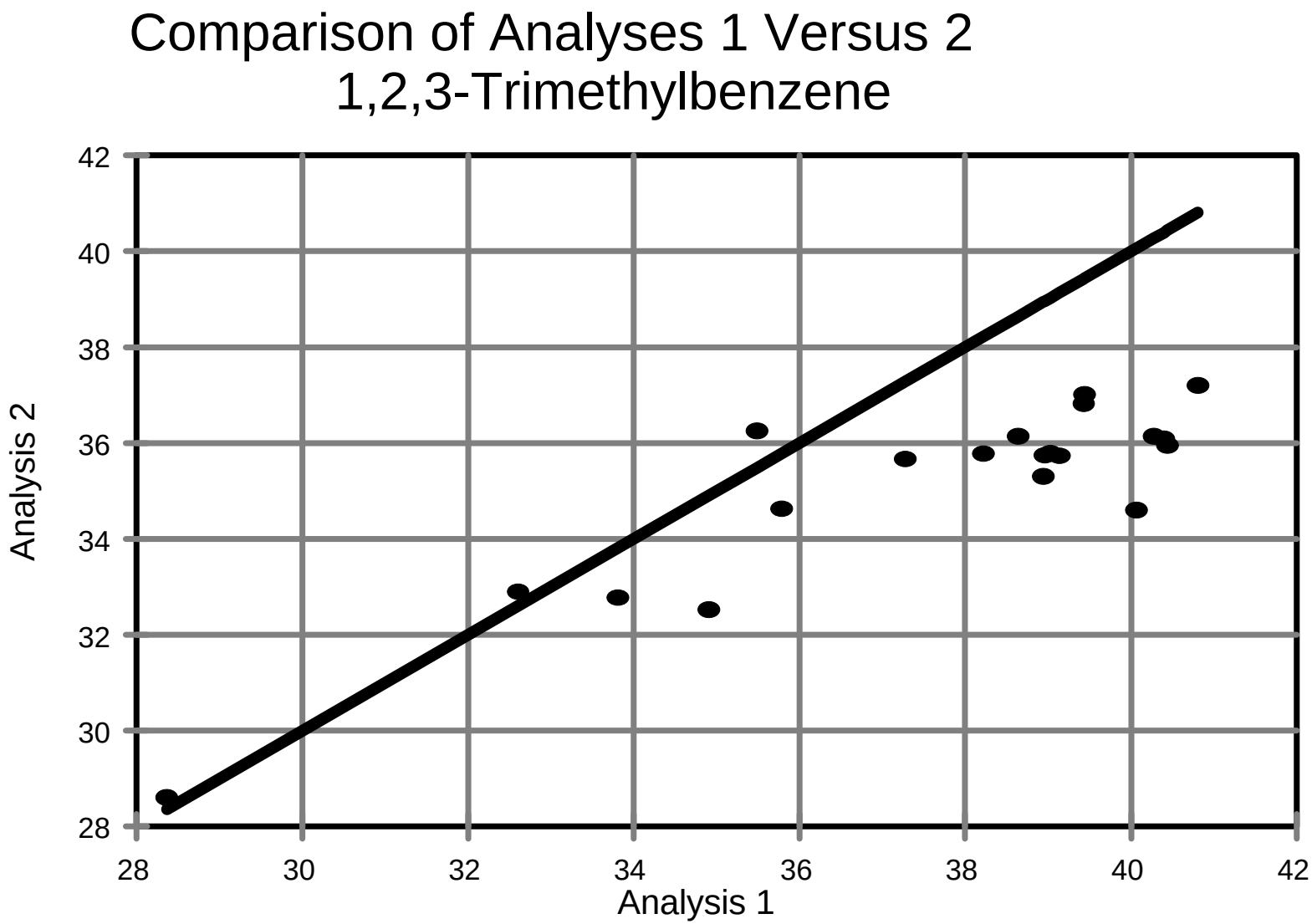

Figure 4-32. Comparison of ERG Analysis 1 to ERG Analysis 2: 1,2,3-Trimethylbenzene

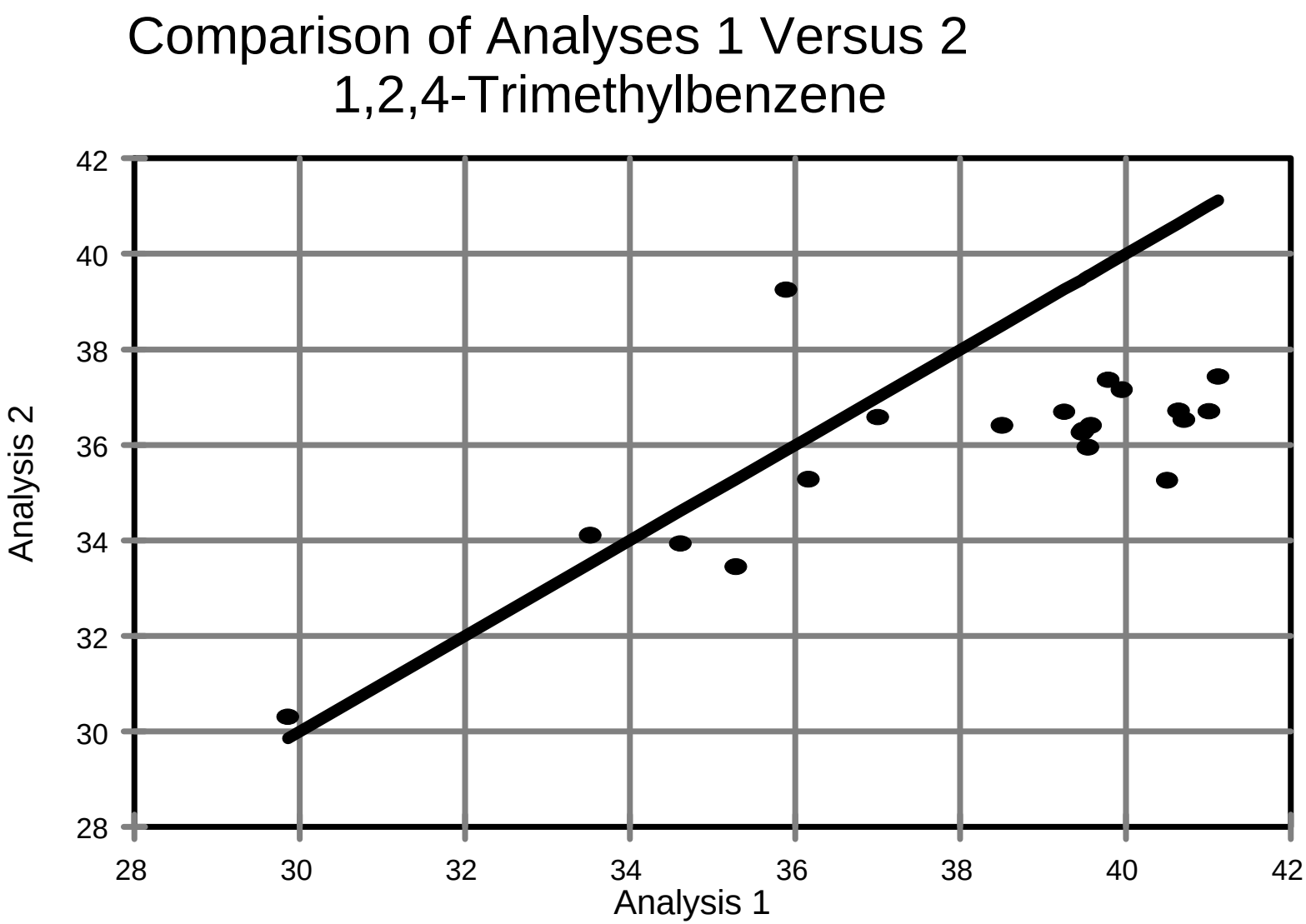

Figure 4-33. Comparison of ERG Analysis 1 to ERG Analysis 2: 1,2,4-Trimethylbenzene

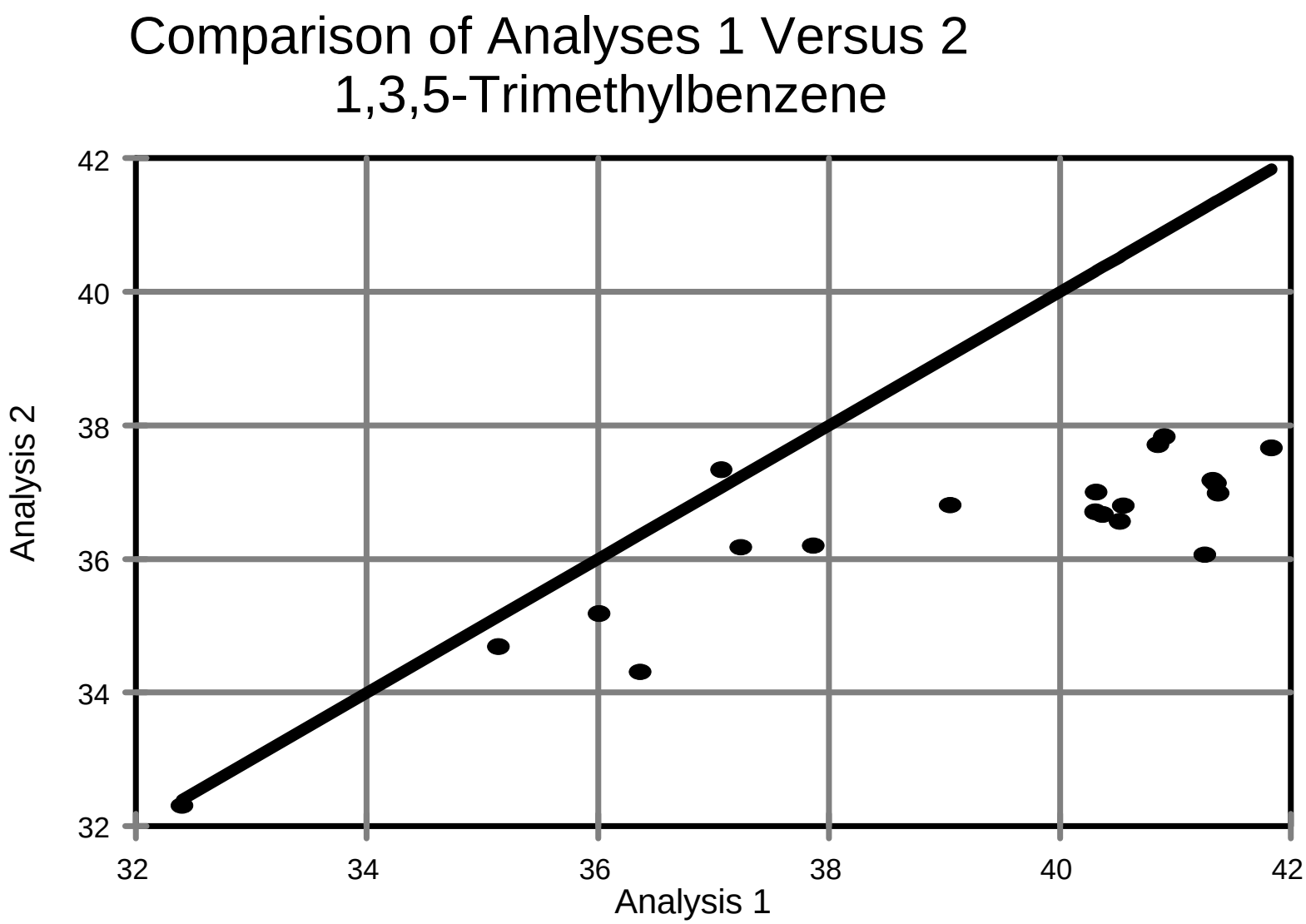

Figure 4-34. Comparison of ERG Analysis 1 to ERG Analysis 2: 1,3,5-Trimethylbenzene

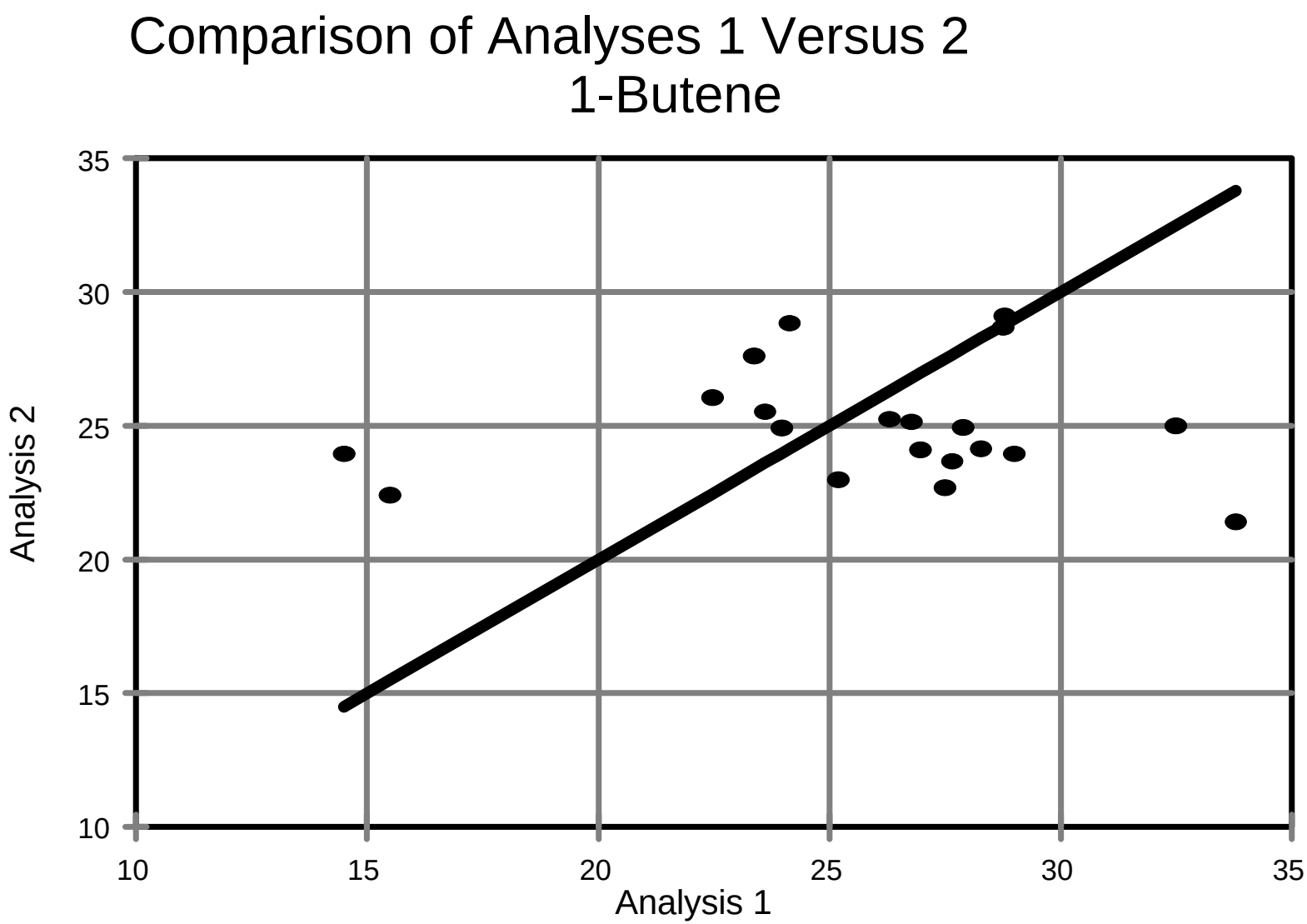

Figure 4-35. Comparison of ERG Analysis 1 to ERG Analysis 2: 1-Butene

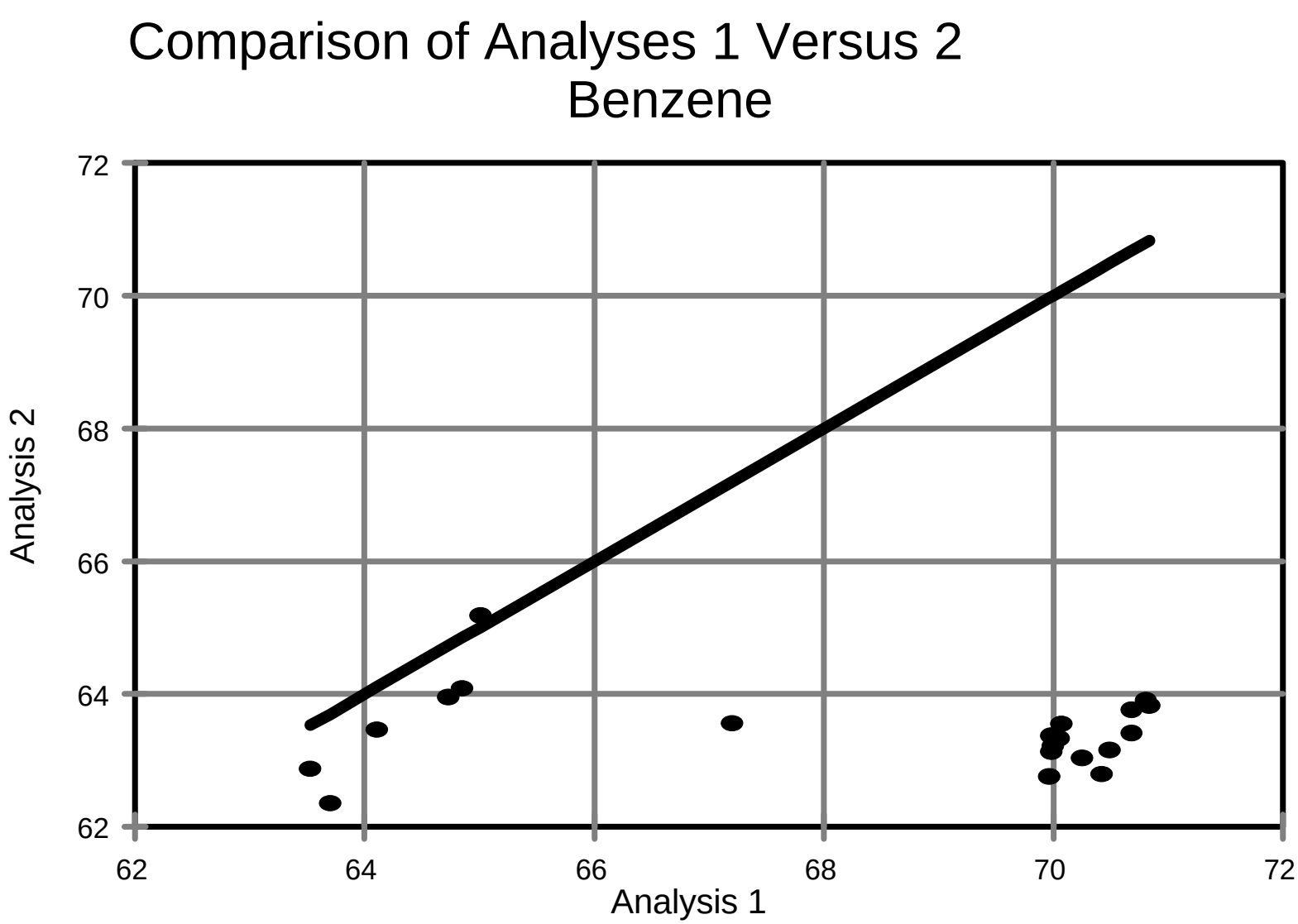

Figure 4-36. Comparison of ERG Analysis 1 to ERG Analysis 2: Benzene

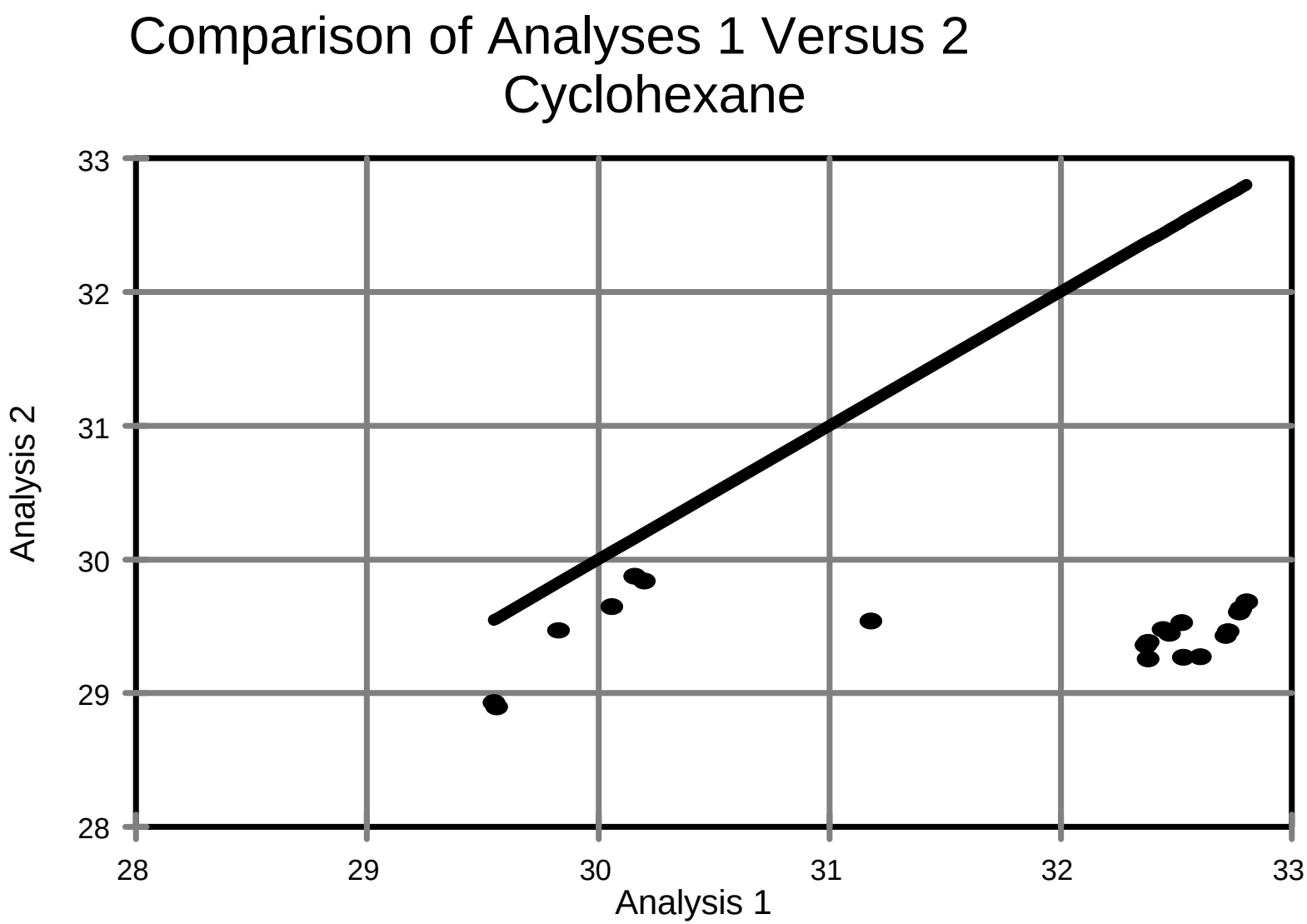

Figure 4-37. Comparison of ERG Analysis 1 to ERG Analysis 2: Cyclohexane

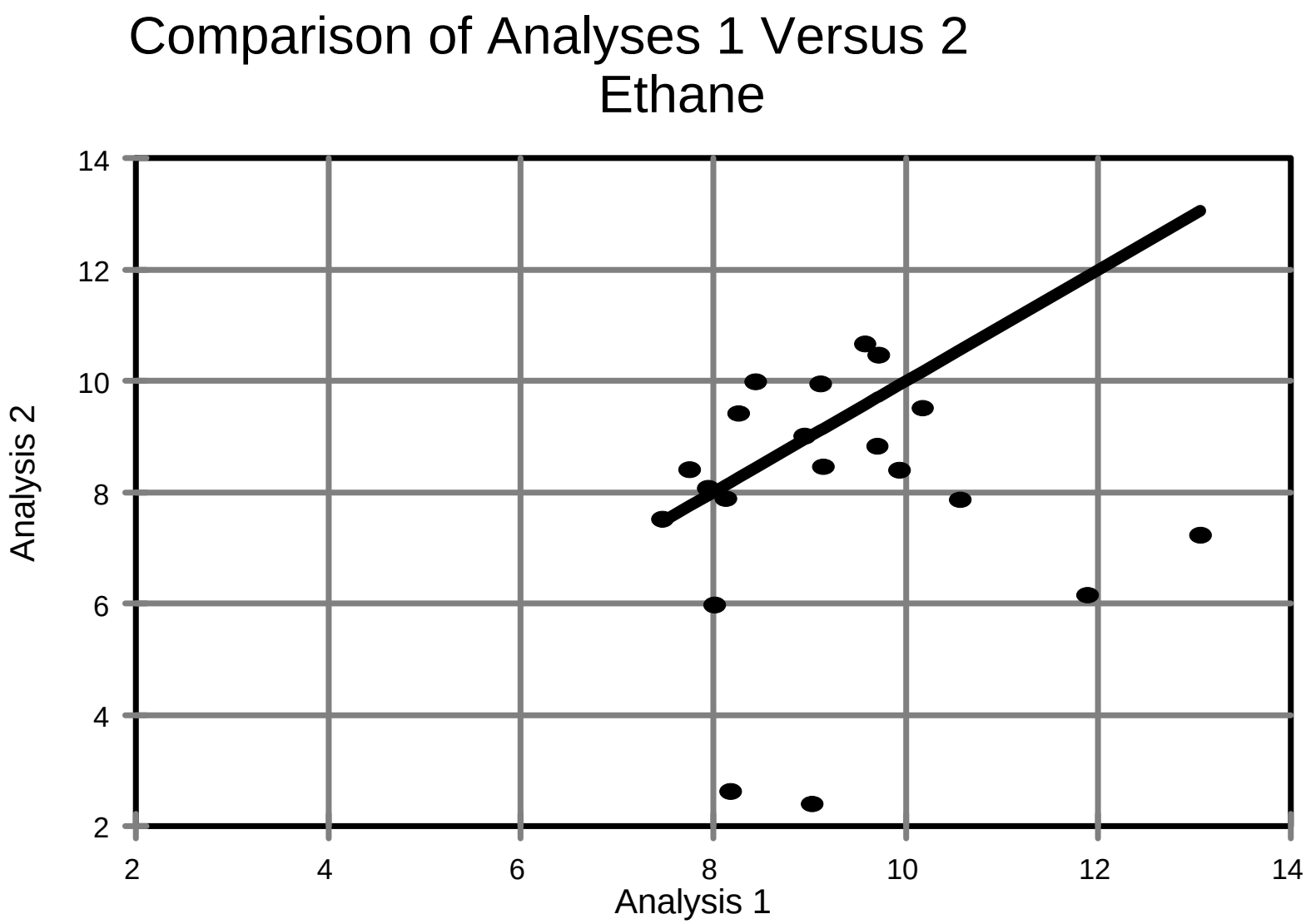

Figure 4-38. Comparison of ERG Analysis 1 to ERG Analysis 2: Ethane

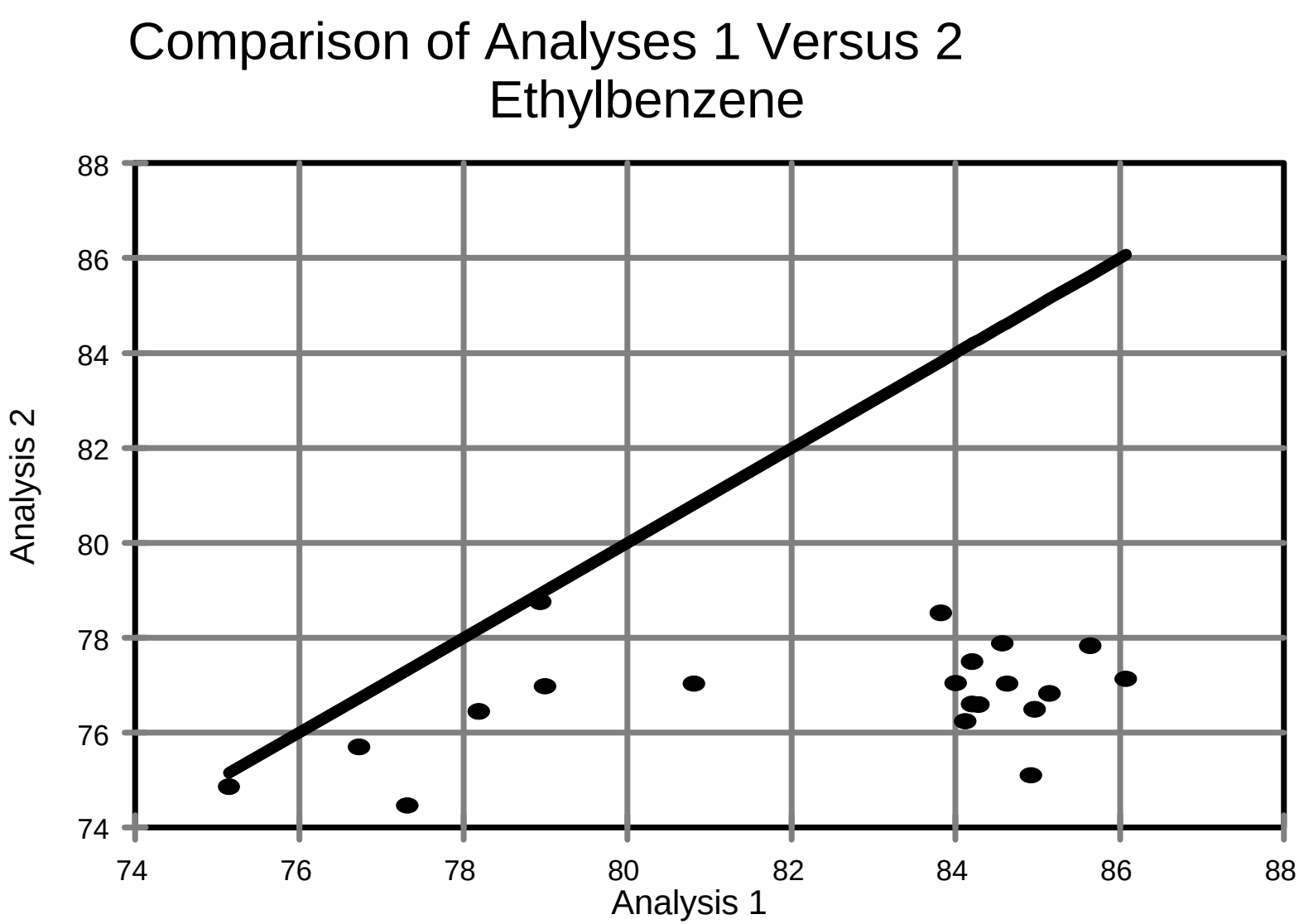

Figure 4-39. Comparison of ERG Analysis 1 to ERG Analysis 2: Ethylbenzene

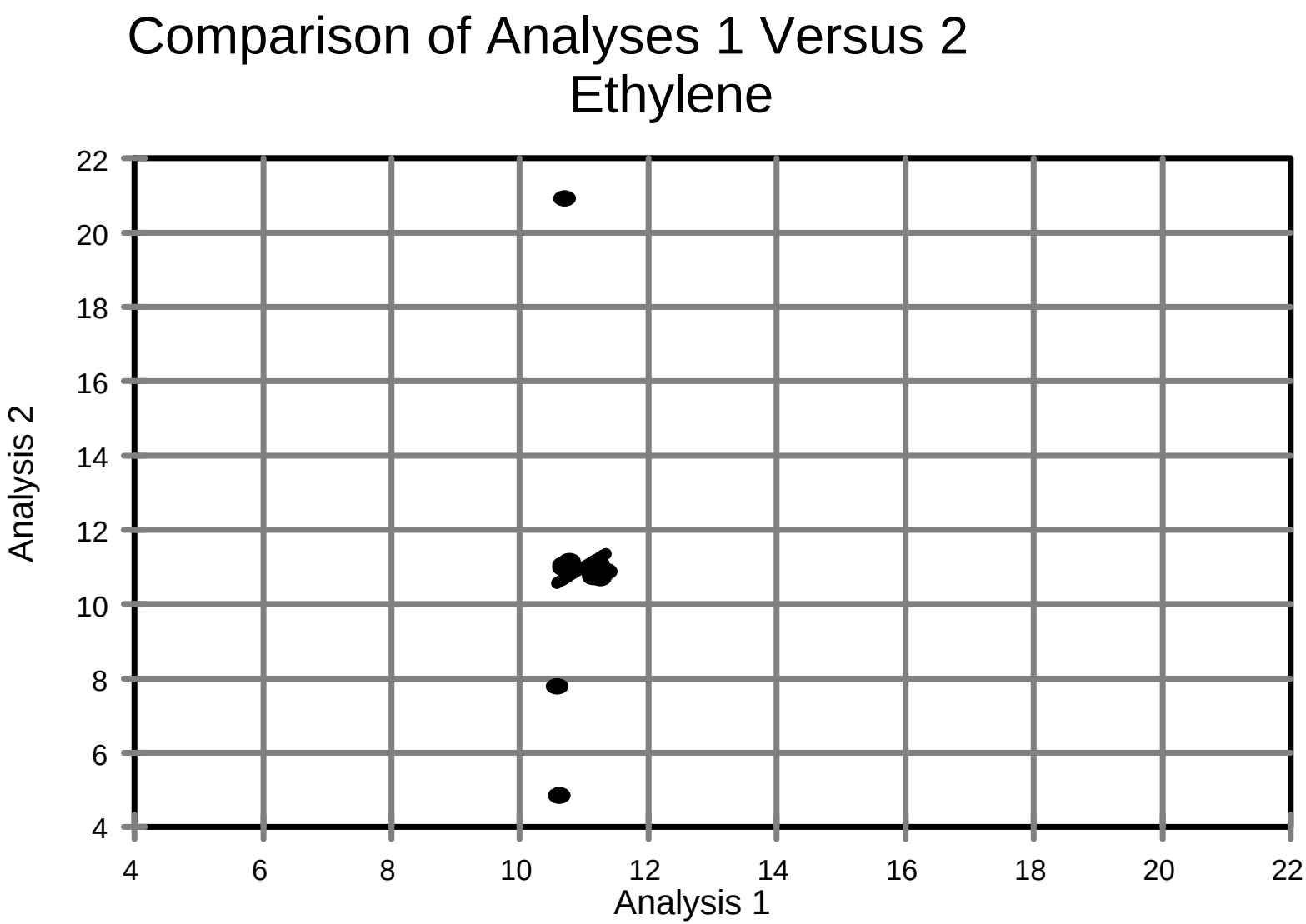

Figure 4-40. Comparison of ERG Analysis 1 to ERG Analysis 2: Ethylene

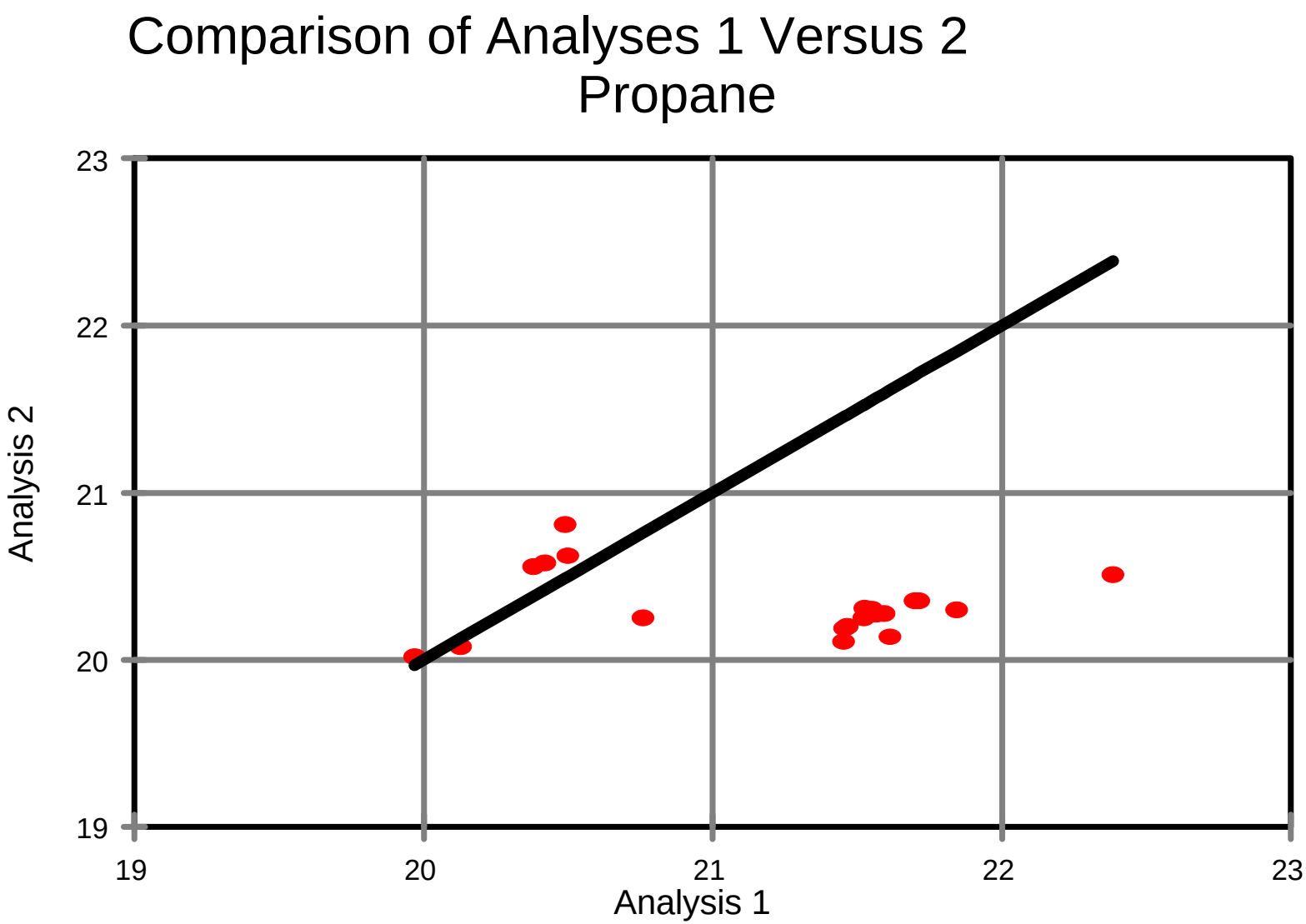

Figure 4-41. Comparison of ERG Analysis 1 to ERG Analysis 2: Propane

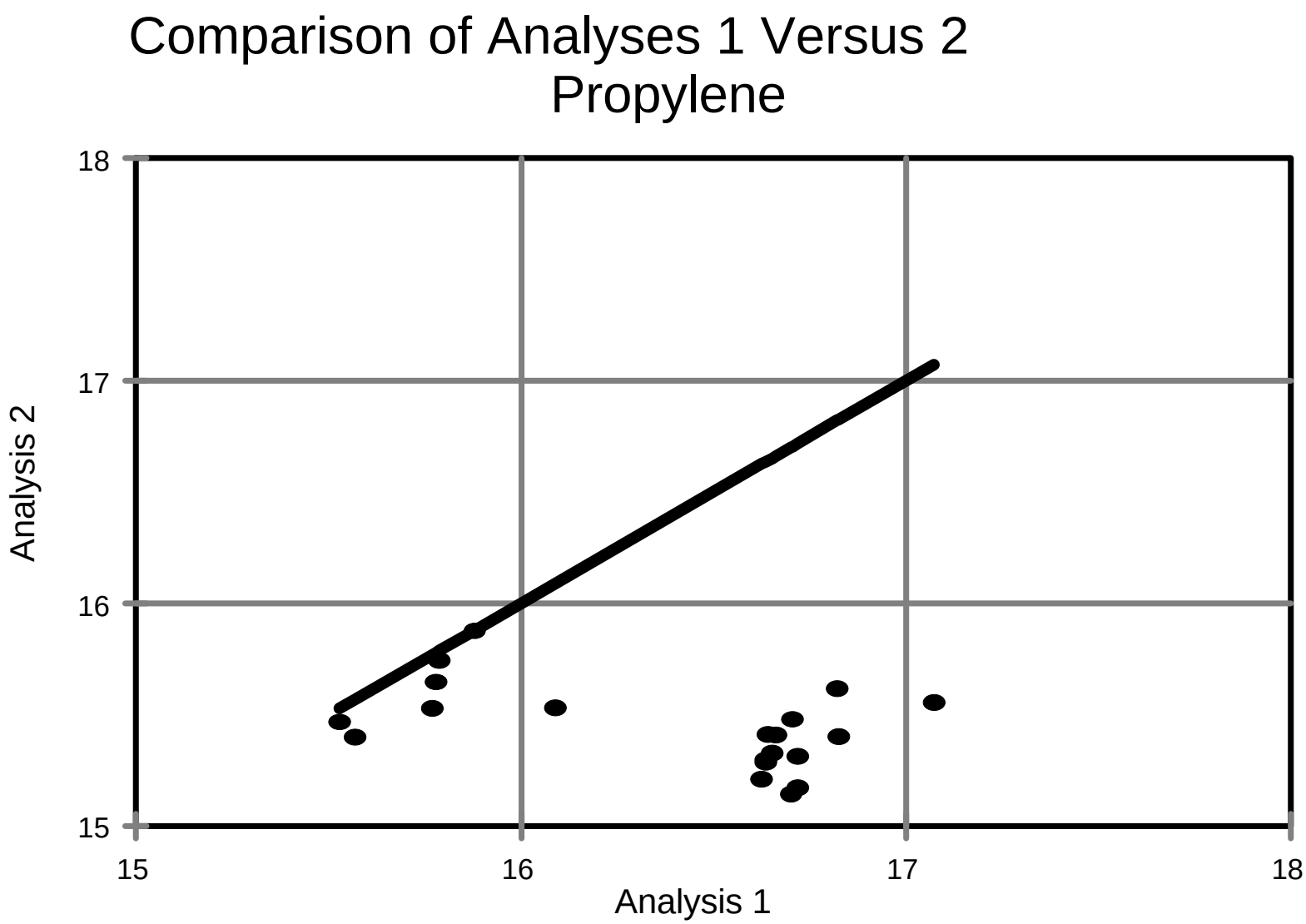

Figure 4-42. Comparison of ERG Analysis 1 to ERG Analysis 2: Propylene

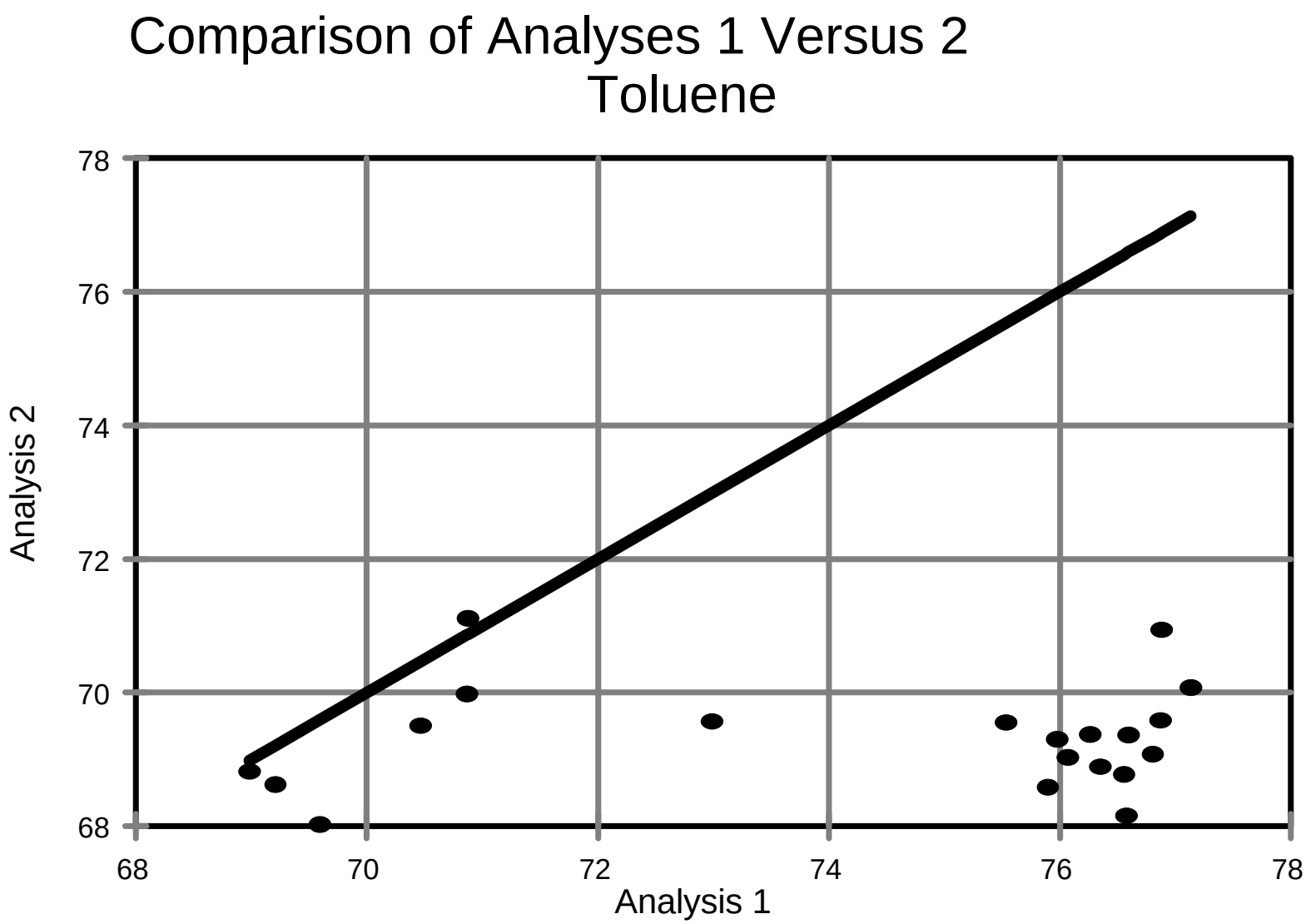

Figure 4-43. Comparison of ERG Analysis 1 to ERG Analysis 2: Toluene

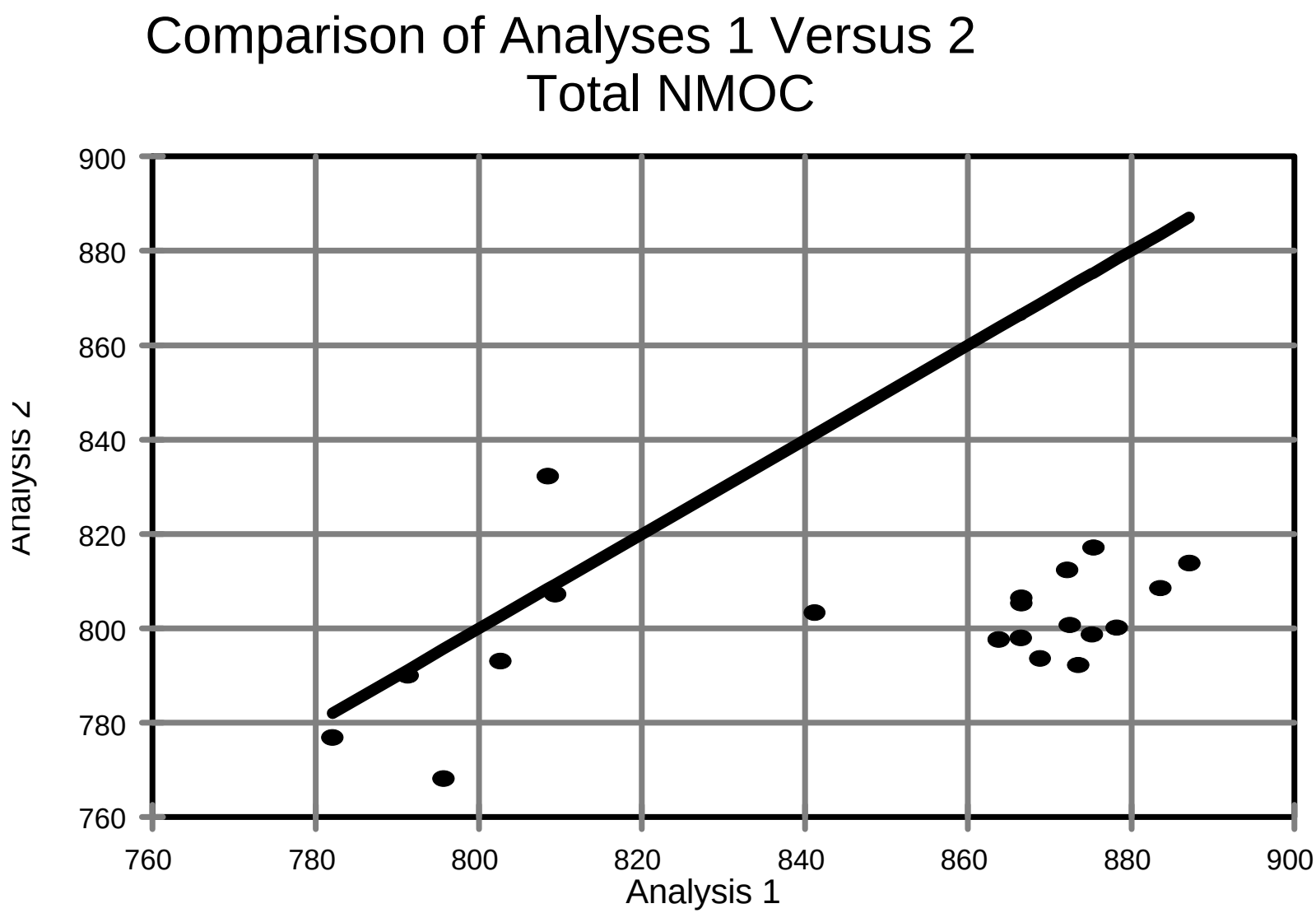

Figure 4-44. Comparison of ERG Analysis 1 to ERG Analysis 2: Total NMOC

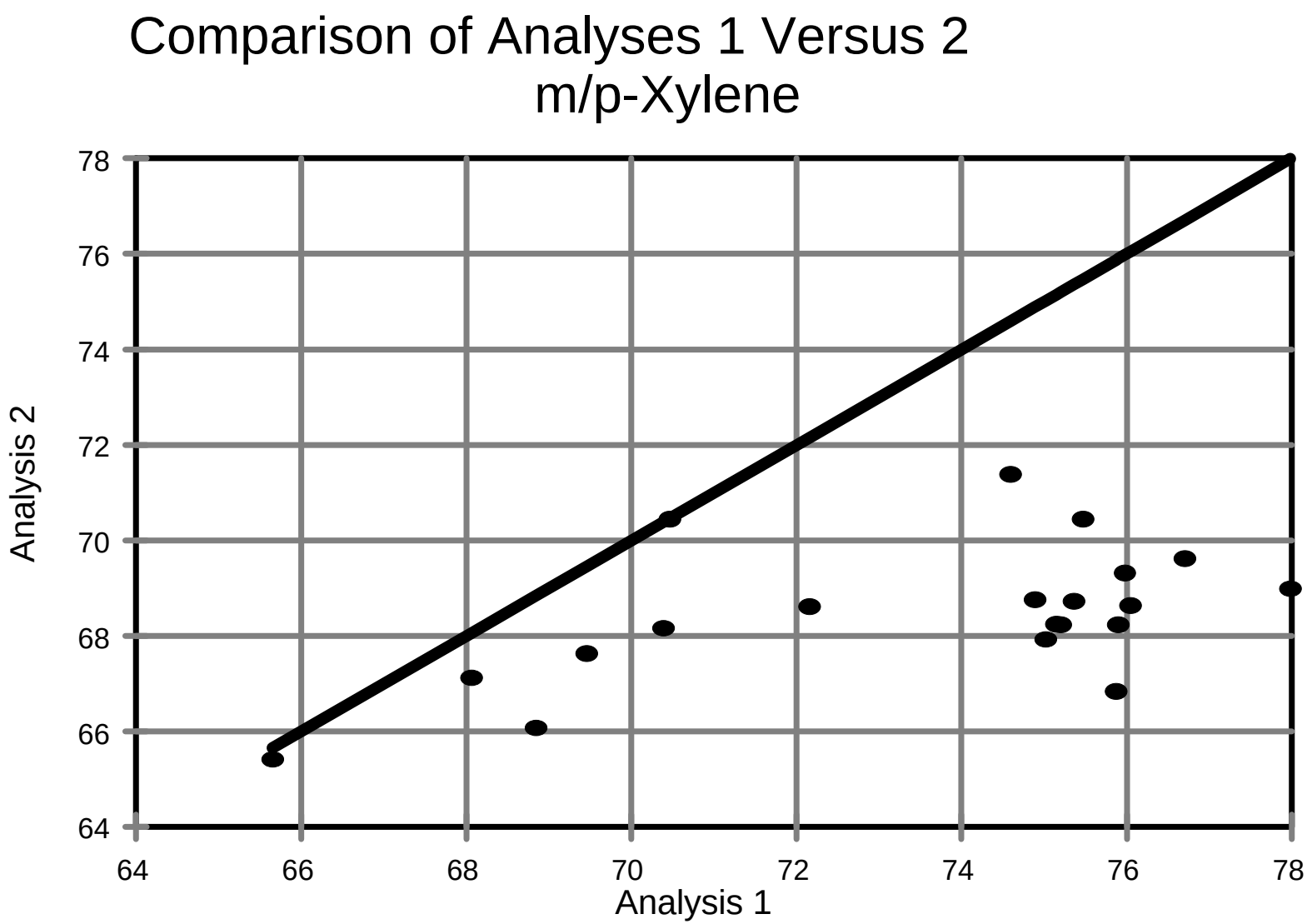

Figure 4-45. Comparison of ERG Analysis 1 to ERG Analysis 2: *m/p*-Xylene

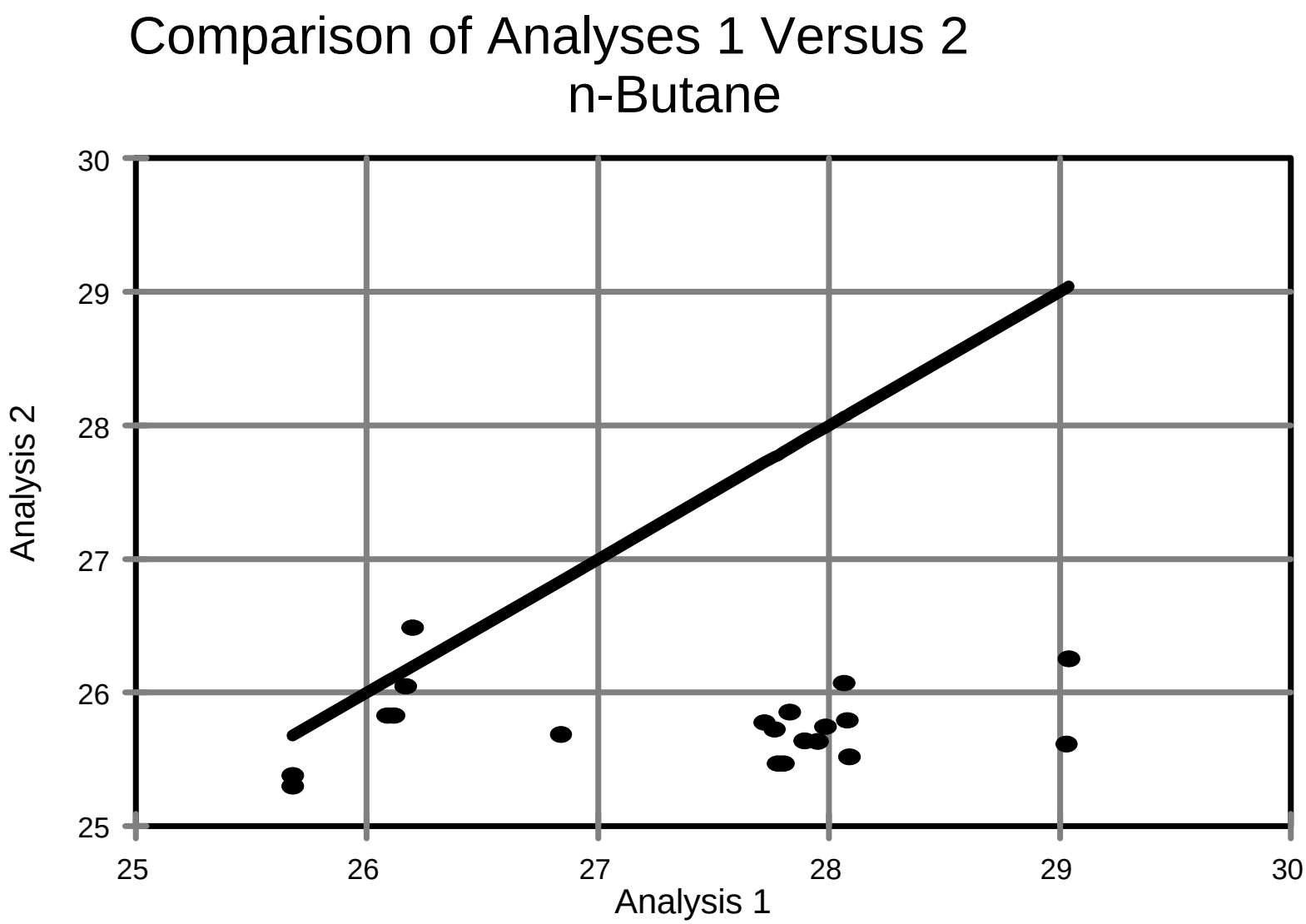

Figure 4-46. Comparison of ERG Analysis 1 to ERG Analysis 2: *n*-Butane

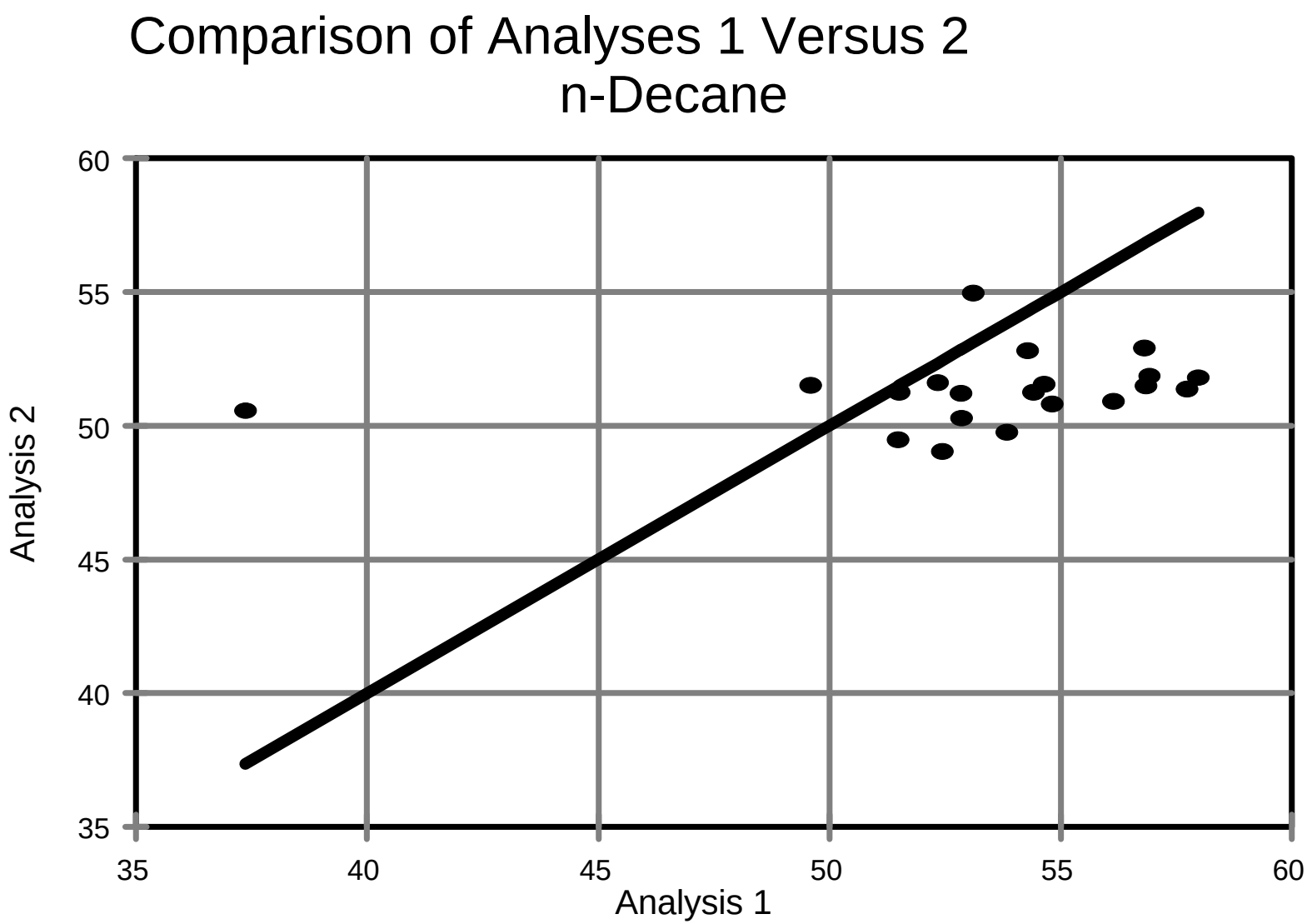

Figure 4-47. Comparison of ERG Analysis 1 to ERG Analysis 2: *n*-Decane

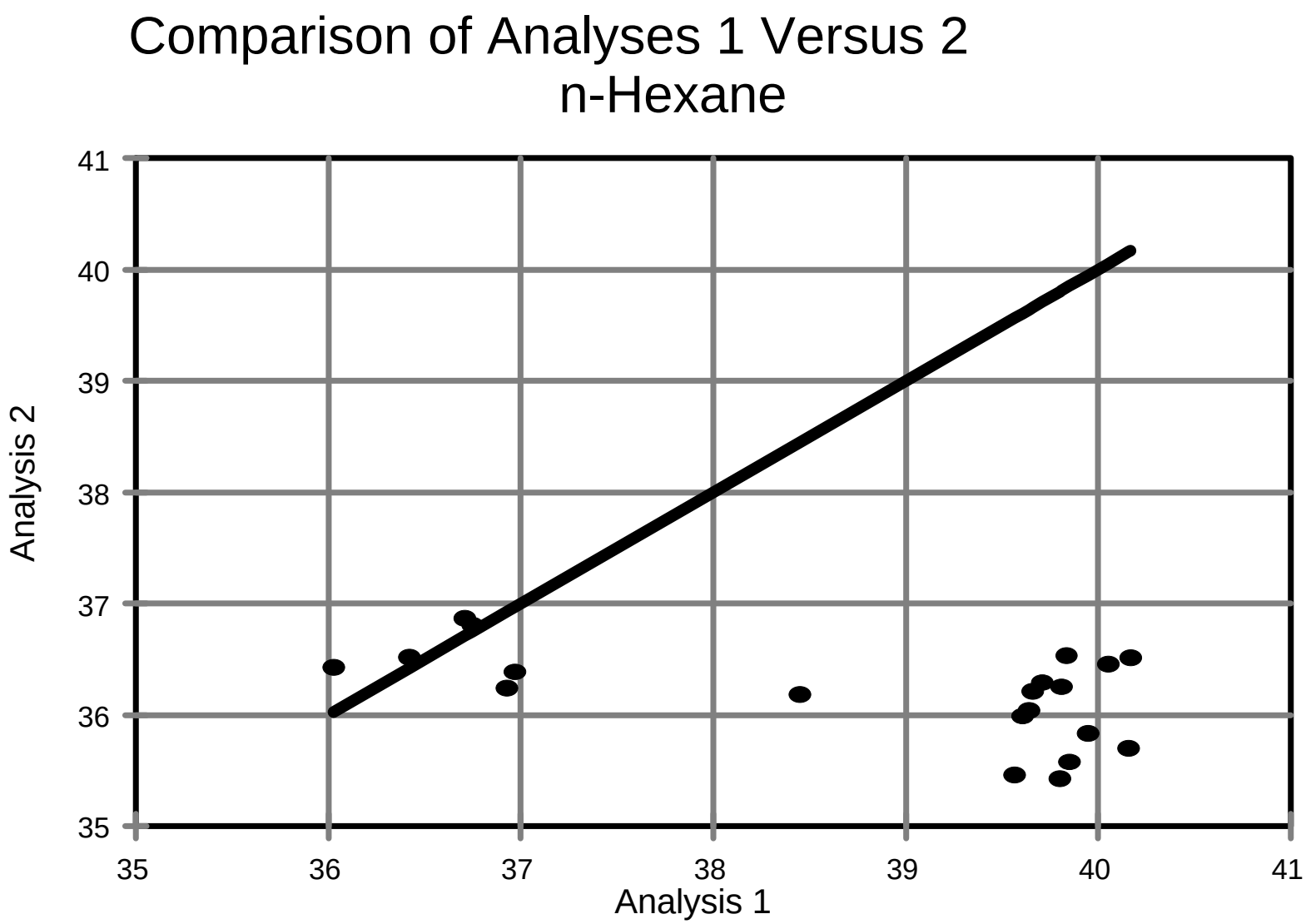

Figure 4-48. Comparison of ERG Analysis 1 to ERG Analysis 2: *n*-Hexane

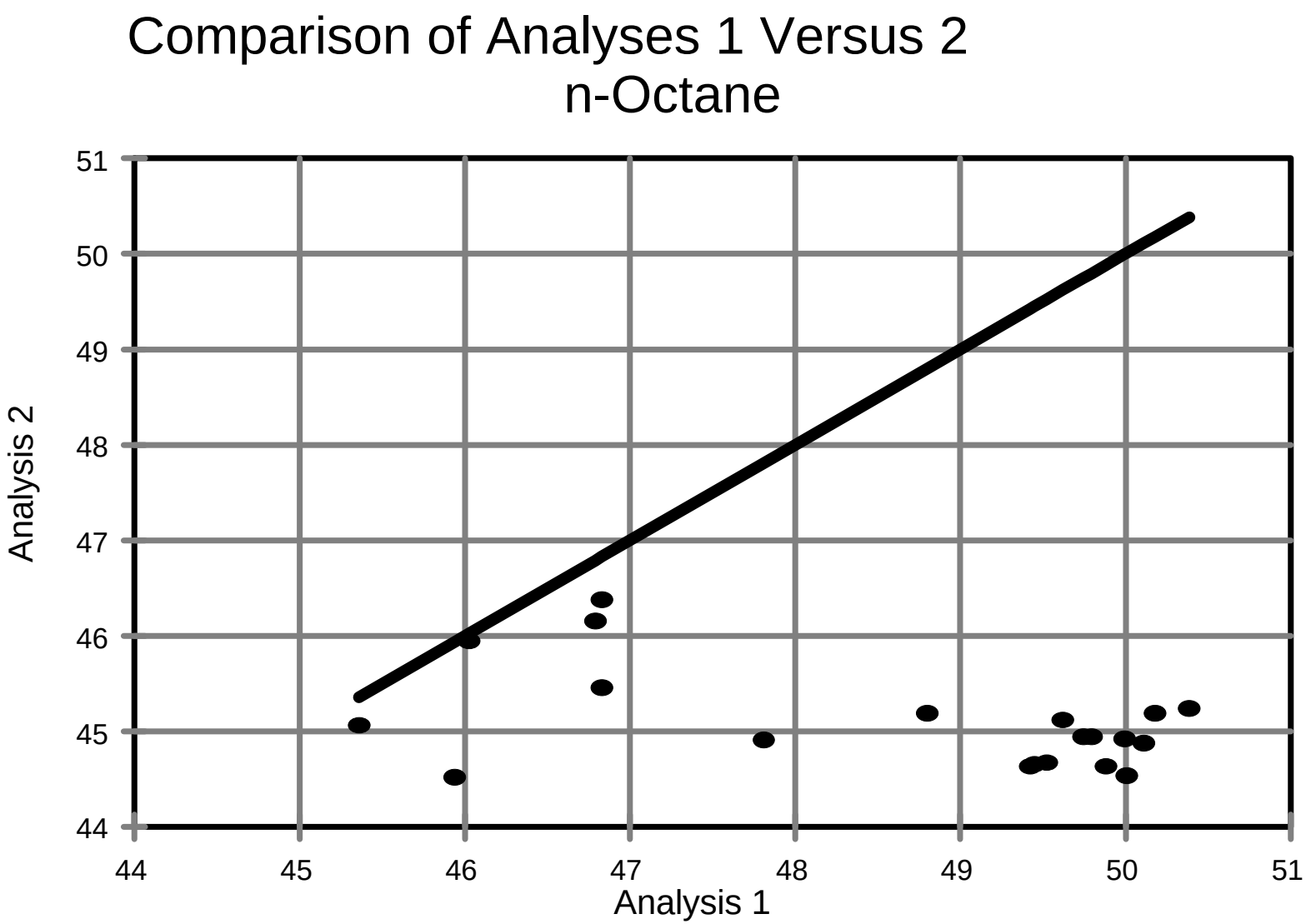

Figure 4-49. Comparison of ERG Analysis 1 to ERG Analysis 2: *n*-Octane

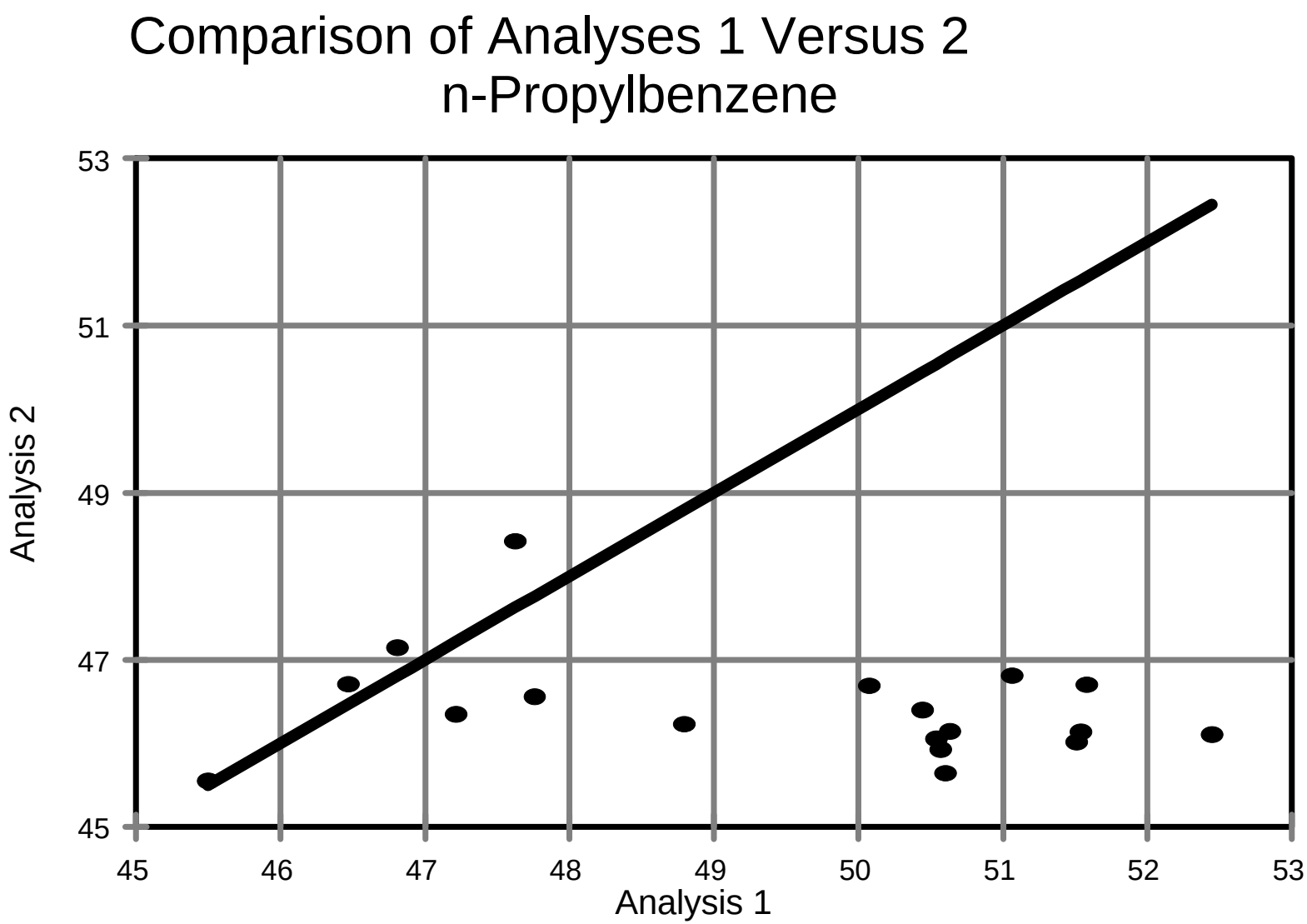

Figure 4-50. Comparison of ERG Analysis 1 to ERG Analysis 2: *n*-Propylbenzene

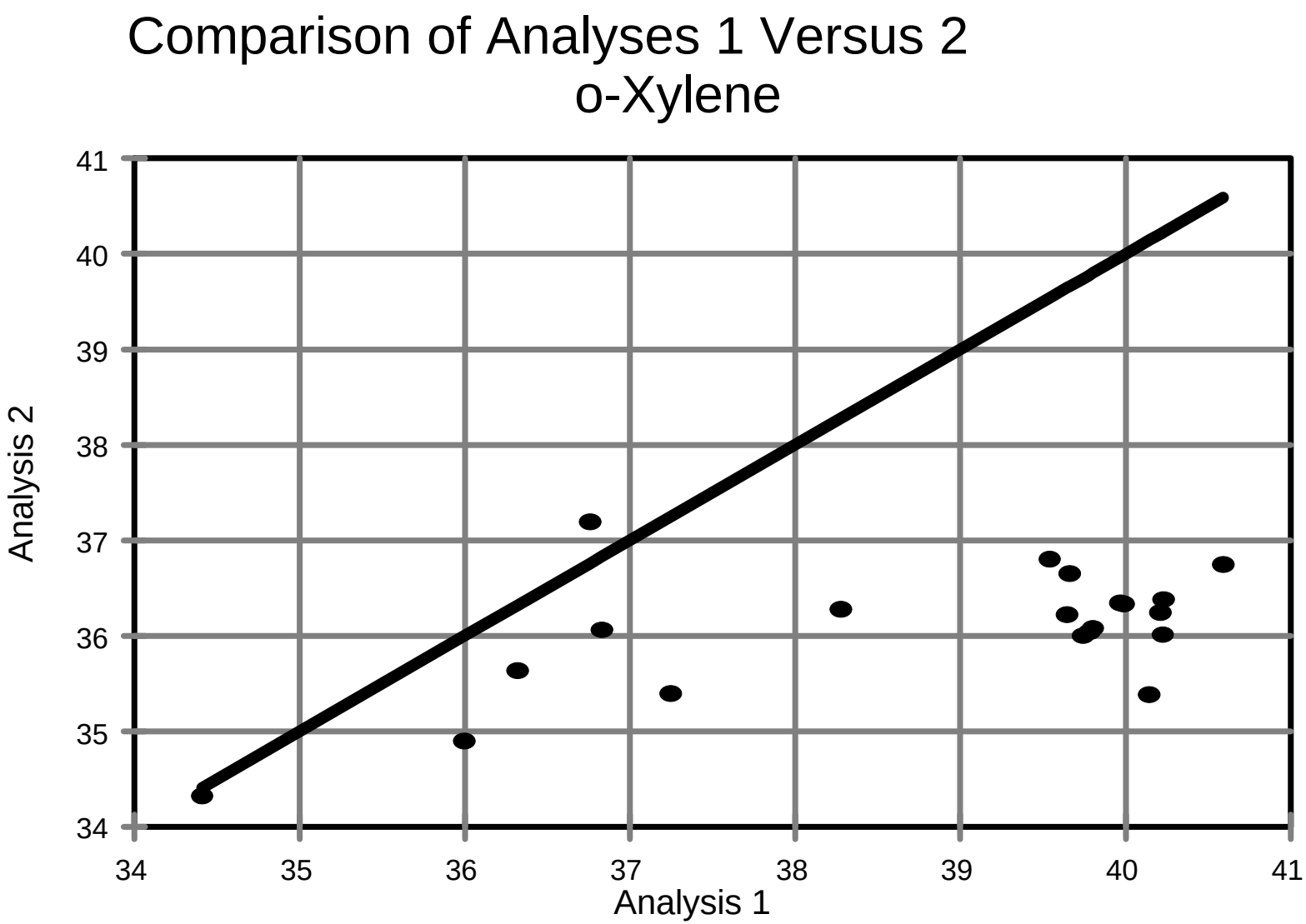

Figure 4-51. Comparison of ERG Analysis 1 to ERG Analysis 2: *o*-Xylene

Table 4-13

Compounds Most Frequently Not Reported by PAMS Sites

Compound	Maximum Possible Data Points	Number of Reported Values
1,2,3-trimethylbenzene	98	88
1,2,4-trimethylbenzene	98	96
1,3,5-trimethylbenzene	98	98
1-butene	98	97
benzene	99	99
cyclohexane	98	98
ethane	98	91
ethylbenzene	98	98
ethylene	98	90
propane	99	99
propylene	98	95
toluene	99	99
m-/*p*-xylene	98	98
n-butane	99	99
n-decane	98	91
n-hexane	98	98
n-octane	99	99
n-propylbenzene	98	96
o-xylene	98	98
Total NMOC	98	95

The compound reported least frequently (i.e., missed in the analysis most frequently; reported in 88 out of 98 datasets) was 1,2,3-trimethylbenzene, a late-eluting compound. Next lowest in order of frequency of reporting was ethylene (reported in 90 out of 98 datasets), followed by ethane and *n*-decane (both reported in 91 out of 98 datasets). The compounds most likely not to be reported in the analysis occurred at the early and late extremes of chromatographic elution.

The reproducibility of the measurement by compound for all of the PAMS sites is shown in Table 4-14. The compound name, the number of values in the database, and the standard deviation of the absolute bias is presented. Compounds with the highest values for standard deviation of the absolute bias showed the widest range in the reported measurements.

Compounds with the highest standard deviation (>15) were: 1,2,3-trimethylbenzene, 1-butene, and *n*-decane. Two of these compounds, 1,2,3-trimethylbenzene and *n*-decane, were also compounds that were not reported several times in the 98 datasets. A reason why these particular compounds should be both more difficult to find and more difficult to quantify accurately is not obvious.

A summary of the statistical calculations by compound compared to the mean of the reported values from the PAMS sites (excluding zeroes and outliers) is shown in Table 4-15. A summary of the statistical calculations for laboratory bias (both positive and negative bias), arranged according to laboratory, is shown in Table 4-16, with a graphic presentation of the overall average percent bias shown in Figure 4-52. If the magnitude (i.e., absolute value) of the bias is considered, summary statistics by laboratory are shown in Table 4-17 and are presented graphically in Figure 4-53. The overall mean bias (considering bias as a signed value) is -0.25, very nearly zero, whereas the overall mean absolute bias (considering only the magnitude of the bias) is 11.31. Thus, on the whole, an individual PAMS site was within approximately 10% of the mean value of all the PAMS data points.

Table 4-14

Reproducibility of the PAMS Measurements by Compound

Compound	Number of Reported Values	Standard Deviation of Absolute Bias
1,2,3-trimethylbenzene	88	16.62
1,2,4-trimethylbenzene	96	11.47
1,3,5-trimethylbenzene	98	8.18
1-butene	97	18.63
benzene	99	11.67
cyclohexane	98	7.21
ethane	91	13.73
ethylbenzene	98	6.63
ethylene	90	13.91
propane	99	11.00
propylene	95	9.62
toluene	99	9.13
m-/*p*-xylene	98	14.41
n-butane	99	9.61
n-decane	91	20.60
n-hexane	98	13.65
n-octane	99	7.20
n-propylbenzene	96	8.41
o-xylene	98	6.95
Total NMOC	95	8.32

Table 4-15

Statistical Calculations by Compound Compared to the Mean of the Reported Values from the PAMS Sites, Excluding Zeros and Outliers

COMPOUND	N[1]	MEANCONC[2]	STDCONC[3]	CVCONC[4]	LO90CONC[5]	UP90CONC[6]
1,2,3-trimethylbenzene	88	44.66	10.13	22.68	42.86	46.45
1,2,4-trimethylbenzene	96	43.99	7.56	17.18	42.71	45.27
1,3,5-trimethylbenzene	98	43.77	5.51	12.59	42.84	44.69
1-butane	97	26.18	6.12	23.38	25.15	27.21
benzene	99	74.66	11.19	14.98	72.79	76.53
cyclohexane	98	34.59	3.77	10.91	33.96	35.22
ethane	91	13.11	2.45	18.67	12.68	13.53
ethylbenzene	98	95.32	9.75	10.23	93.68	96.95
ethylene	90	10.69	2.04	19.11	10.33	11.05
propane	99	20.83	3.19	15.31	20.30	21.37
propylene	95	17.51	2.26	12.93	17.12	17.89
toluene	99	84.30	10.59	12.57	82.54	86.07
Total NMOC	95	958.77	119.50	12.46	938.41	979.14
m/p-xylene	98	81.22	15.46	19.04	78.62	83.81
n-butane	99	28.66	3.74	13.06	28.04	29.29
n-decane	91	57.45	16.82	29.28	54.52	60.38
n-hexane	98	41.54	7.04	16.95	40.36	42.72
n-octane	99	54.02	5.90	10.92	53.03	55.00
n-propylbenzene	96	58.15	7.02	12.08	56.96	59.34
o-xylene	98	44.45	4.45	10.01	43.70	45.20
ALL	1,922	91.46	201.11	219.88	83.92	99.01

[1] Sample size (number) of datasets reporting this compound.
[2] Arithmetic average.
[3] Standard deviation.
[4] Coefficient of variation: (STD/MEAN) x 100.
[5] Lower 90% confidence bound.
[6] Upper 90% confidence bound.
[7] Lower 95% confidence bound.
[8] Upper 95% confidence bound.
[9] The mean of the signed bias values is zero.
[10] The mean of the magnitude of the bias values is a non-zero value.

Table 4-15
Continued

COMPOUND	LO95CONC[7]	UP95CONC[8]	MEANB[2,9]	STDBIAS[3]	MEANABS[2,10]	STDABS[3]
1,2,3-trimethylvenzene	42.51	46.80	0.00	22.68	15.35	16.62
1,2,4-trimethylbenzene	42.46	45.52	0.00	17.18	12.72	11.47
1,3,5-trimethylbenzene	42.66	44.87	0.00	12.59	9.53	8.18
1-butane	24.95	27.41	0.00	23.38	14.05	18.63
benzene	72.43	76.89	0.00	14.98	9.35	11.67
cyclohexane	33.83	35.35	0.00	10.91	8.15	7.21
ethane	12.60	13.62	0.00	18.67	12.58	13.73
ethylbenzene	93.36	97.27	0.00	10.23	7.76	6.63
ethylene	10.26	11.12	0.00	19.11	13.03	13.91
propane	20.20	21.47	0.00	15.31	10.60	11.00
proplene	17.05	17.97	0.00	12.93	8.60	9.62
toluene	82.19	86.42	0.00	12.57	8.59	9.13
Total NMOC	934.43	983.12	0.00	12.46	9.23	8.32
m/p-xylene	78.12	84.32	0.00	19.04	12.39	14.41
n-butane	27.91	29.41	0.00	13.06	8.80	9.61
n-decane	53.94	60.95	0.00	29.28	20.68	20.60
n-hexane	40.13	42.95	0.00	16.95	9.99	13.65
n-octane	52.84	55.19	0.00	10.92	8.17	7.20
n-propylbenzene	56.72	59.57	0.00	12.08	8.62	8.41
o-xylene	43.56	45.34	0.00	10.01	7.17	6.95
ALL	82.47	100.46	0.00	16.28	10.69	12.28

[1] Sample size (number) of datasets reporting this compound.
[2] Arithmetic average.
[3] Standard deviation.
[4] Coefficient of variation: (STD/MEAN) x 100.
[5] Lower 90% confidence bound.
[6] Upper 90% confidence bound.
[7] Lower 95% confidence bound.
[8] Upper 95% confidence bound.
[9] The mean of the signed bias values is zero.
[10] The mean of the magnitude of the bias values is a non-zero value.

Table 4-16

Summary of Statistical Calculations by Laboratory

LAB	N[1]	MEANBIAS[2]	STD[3]	CV[4]	NORMSTAT[5]	PROBNORM[6]	MIN[7]	Q1[8]	MEDIAN[9]	Q3[10]	MAX[11]
1	40	-12.04	6.72	-55.84	0.89	0.00	-27.97	-15.42	-12.89	-9.79	6.57
2	80	-10.60	19.52	-184.25	0.61	0.00	-98.26	-8.39	-5.03	-1.73	21.84
3	40	-5.45	7.49	-137.39	0.81	0.00	-14.47	-9.35	-7.67	-4.00	19.21
4	80	0.63	6.79	1083.91	0.95	0.01	-21.70	-3.00	1.18	5.38	13.15
5	40	4.32	5.57	128.97	0.97	0.54	-10.20	0.79	4.46	6.75	16.98
6	80	16.68	28.20	169.09	0.93	0.00	-68.03	4.49	14.91	32.70	88.10
7	40	2.41	4.88	202.49	0.79	0.00	-20.50	0.56	2.41	5.69	8.70
8	60	2.30	8.70	377.79	0.96	0.10	-14.40	-3.29	1.13	6.53	19.78
9	80	-3.60	11.86	-329.63	0.95	0.01	-46.68	-7.93	-3.07	1.90	33.43
10	36	-2.15	20.40	-947.22	0.96	0.28	-47.06	-10.83	-3.61	9.76	45.65
11	78	-22.02	14.88	-67.60	0.69	0.00	-98.47	-26.22	-21.67	-14.71	7.81
12	60	9.66	11.78	122.02	0.93	0.00	-10.72	-2.05	10.73	19.02	30.57
13	40	-7.32	26.95	-367.98	0.80	0.00	-95.13	-10.57	-1.44	9.12	24.52
14	57	4.35	10.61	244.16	0.95	0.05	-22.54	-0.04	2.56	9.95	25.90
15	57	4.34	7.76	178.71	0.93	0.01	-12.62	-0.65	1.82	8.13	23.62
16	120	2.41	6.66	275.95	0.93	0.00	-23.39	-0.87	3.48	6.35	14.14
17	38	-6.86	7.77	-113.19	0.73	0.00	-40.79	-8.39	-6.03	-3.23	3.75
19	115	1.78	6.23	349.69	0.98	0.28	-15.81	-2.33	1.10	5.49	23.07

[1] N = number of data points submitted by the PAMS site. PAMS sites were requested to perform and report replicate determinations (i.e., 40 data points). Some PAMS sites performed multiple sets of replicate analyses on different instruments.
[2] MEANBIAS = arithmetic mean of bias values for all compounds reported by the particular PAMS sites.
[3] STD = sample standard deviation.
[4] CV = coefficient of variation = (STD/MEAN) x 100.
[5] NORMSTAT = normality statistic (from SAS, for sample sizes<2000). This is the Shapiro-Wilk "w" statistic which tests the null hypothesis that the data sample comes from a normal data distribution.
[6] PROBNORM = probability level for NORMSTAT (from SAS, for samples sizes <2000, probability of a smaller "w" statistic). For the data distribution to be considered NORMAL, the probability level must be 0.05 or larger for a 95% confidence level (accept the null hypothesis).
[7] MIN = minimum value from sample.
[8] Q1 = 25th percentile from sample.
[9] MEDIAN = 50th percentile from sample.
[10] Q3 = 75th percentile from sample.
[11] MAX = maximum value from sample.

Table 4-16
Continued

LAB	N[1]	MEANBIAS[2]	STD[3]	CV[4]	NORMSTAT[5]	PROBNORM[6]	MIN[7]	Q1[8]	MEDIAN[9]	Q3[10]	MAX[11]
20	36	-0.55	22.83	-4167.66	0.83	0.00	-86.57	-3.61	1.61	14.19	27.97
22	40	5.55	7.96	143.38	0.95	0.11	-7.20	-0.35	3.99	10.70	22.20
23	40	-13.72	10.69	-77.86	0.93	0.01	-43.47	-22.84	-13.43	-5.29	11.76
24	80	2.45	10.51	429.31	0.89	0.00	-36.13	-1.97	4.86	8.02	21.51
25	36	21.40	10.22	47.75	0.98	0.80	0.02	16.25	21.45	27.85	41.92
26	40	3.19	8.74	274.00	0.95	0.08	-9.91	-3.46	1.44	8.67	26.24
27	40	10.23	14.97	146.34	0.77	0.00	-44.03	6.15	11.83	17.33	37.03
28	40	10.23	6.27	61.26	0.98	0.86	-4.07	5.81	10.00	14.64	21.98
29	40	3.19	6.64	208.42	0.96	0.23	-7.76	-1.26	3.12	8.07	16.27
30	38	-2.06	15.42	-750.21	0.96	0.22	-44.23	-12.05	-4.25	4.68	35.23
31	40	-10.62	4.59	-43.16	0.95	0.08	-22.12	-13.03	-10.23	-8.08	-2.70
32	52	1.80	25.96	1442.15	0.75	0.00	-91.82	-1.67	8.14	15.30	40.51
33	80	0.10	11.96	12027.13	0.84	0.00	-15.83	-9.89	1.26	5.86	66.79
34	80	2.82	10.71	380.13	0.73	0.00	-50.92	-0.51	3.74	8.19	17.97
35	23	-8.69	37.65	-433.22	0.93	0.13	-98.47	-17.91	-1.83	11.21	66.43
36	40	-6.71	5.46	-81.37	0.95	0.09	-15.40	-11.24	-6.70	-3.03	4.66
37	36	-6.62	20.92	-334.19	0.76	0.00	-44.61	-31.31	6.33	9.36	15.25
ALL	**35**	**-0.25**	**8.64**	**-3422.71**	**0.98**	**0.72**	**-22.02**	**-6.71**	**1.78**	**4.32**	**21.40**

[1] N = number of data points submitted by the PAMS site. PAMS sites were requested to perform and report replicate determinations (i.e., 40 data points). Some PAMS sites performed multiple sets of replicate analyses on different instruments.
[2] MEANBIAS = arithmetic mean of bias values for all compounds reported by the particular PAMS sites.
[3] STD = sample standard deviation.
[4] CV = coefficient of variation = (STD/MEAN) x 100.
[5] NORMSTAT = normality statistic (from SAS, for sample sizes<2000). This is the Shapiro-Wilk "w" statistic which tests the null hypothesis that the data sample comes from a normal data distribution.
[6] PROBNORM = probability level for NORMSTAT (from SAS, for samples sizes <2000, probability of a smaller "w" statistic). For the data distribution to be considered NORMAL, the probability level must be 0.05 or larger for a 95% confidence level (accept the null hypothesis).
[7] MIN = minimum value from sample.
[8] Q1 = 25th percentile from sample.
[9] MEDIAN = 50th percentile from sample.
[10] Q3 = 75th percentile from sample.
[11] MAX = maximum value from sample.

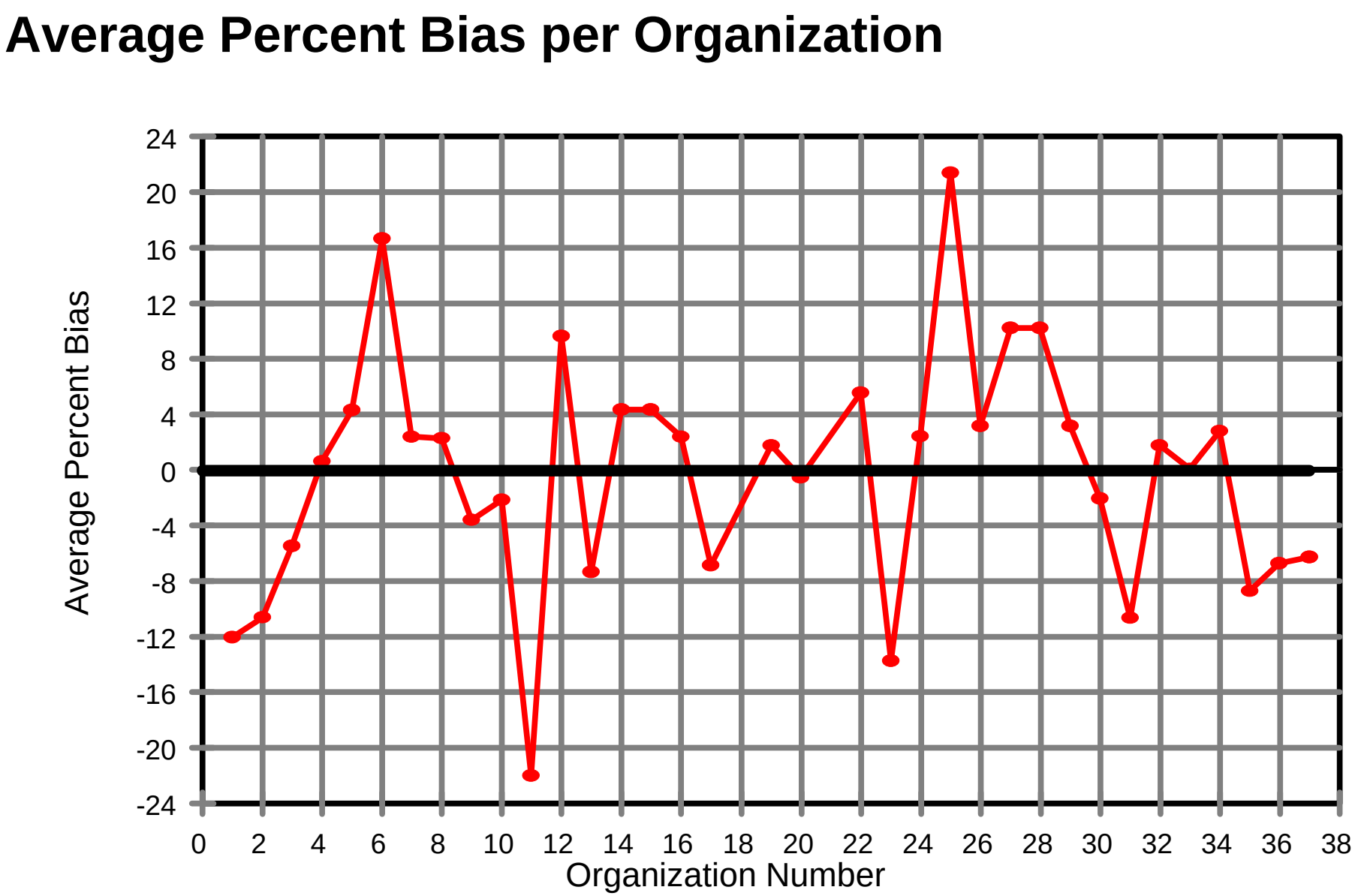

Figure 4-52. Average Percent Bias (Considering Bias Positive or Negative) per Organization for all Compounds

Table 4-17

Summary of Statistical Calculations by Laboratory for Absolute Bias

LAB	N[1]	MEANBIAS[2]	STD[3]	CV[4]	NORMSTAT[5]	PROBNORM[6]	MIN[7]	Q1[8]	MEDIAN[9]	Q3[10]	MAX[11]
1	40	12.68	5.38	42.45	0.93	0.02	0.21	9.79	12.89	15.42	27.97
2	80	11.34	19.09	168.37	0.56	0.00	0.04	2.10	5.20	8.66	98.26
3	40	8.06	4.46	55.31	0.96	0.18	0.13	4.74	8.02	9.84	19.21
4	80	5.31	4.23	79.58	0.88	0.00	0.10	2.53	4.64	7.02	21.70
5	40	5.54	4.33	78.17	0.90	0.00	0.02	2.07	4.59	8.08	16.98
6	80	24.93	21.16	84.86	0.88	0.00	0.03	8.59	17.44	34.91	88.10
7	40	3.99	3.66	91.55	0.79	0.00	0.10	1.40	3.23	5.95	20.50
8	60	7.02	5.57	79.41	0.90	0.00	0.02	2.12	5.55	11.26	19.78
9	80	8.54	8.94	104.74	0.78	0.00	0.02	2.84	4.95	11.40	46.68
10	36	15.25	13.49	88.45	0.80	0.00	0.09	5.97	10.02	20.44	47.06
11	78	22.30	14.45	64.78	0.65	0.00	3.23	14.71	21.67	26.22	98.47
12	60	12.85	8.11	63.15	0.93	0.00	0.79	5.51	11.08	19.02	30.57
13	40	17.16	21.90	127.66	0.69	0.00	0.11	4.96	9.92	18.32	95.13
14	57	8.28	7.88	95.27	0.85	0.00	0.04	1.75	4.63	13.67	25.90
15	57	6.15	6.39	103.97	0.83	0.00	0.04	1.07	4.03	9.43	23.62
16	12	5.54	4.39	79.17	0.89	0.00	0.01	2.36	4.37	7.84	23.39
17	38	7.23	7.42	102.52	0.66	0.00	0.23	3.39	6.03	8.39	40.79
19	11	4.77	4.37	91.70	0.84	0.00	0.04	1.48	3.84	6.62	23.07

[1] N = number of data points submitted by the PAMS site. PAMS sites were requested to perform and report replicate determinations (i.e., 40 data points). Some PAMS sites performed multiple sets of replicate analyses on different instruments.
[2] MEANBIAS = arithmetic mean of bias values for all compounds reported by the particular PAMS sites.
[3] STD = sample standard deviation.
[4] CV = coefficient of variation = (STD/MEAN) x 100.
[5] NORMSTAT = normality statistic (from SAS, for sample sizes<2000). This is the Shapiro-Wilk "w" statistic which tests the null hypothesis that the data sample comes from a normal data distribution.
[6] PROBNORM = probability level for NORMSTAT (from SAS, for samples sizes <2000, probability of a smaller "w" statistic). For the data distribution to be considered NORMAL, the probability level must be 0.05 or larger for a 95% confidence level (accept the null hypothesis).
[7] MIN = minimum value from sample.
[8] Q1 = 25th percentile from sample.
[9] MEDIAN = 50th percentile from sample.
[10] Q3 = 75th percentile from sample.
[11] MAX = maximum value from sample.

Table 4-17
Continued

LAB	N[1]	MEANBIAS[2]	STD[3]	CV[4]	NORMSTAT[5]	PROBNORM[6]	MIN[7]	Q1[8]	MEDIAN[9]	Q3[10]	MAX[11]
20	36	14.59	17.39	119.16	0.76	0.00	0.05	2.90	7.60	20.07	86.57
22	40	7.29	6.36	87.31	0.88	0.00	0.05	2.16	5.21	10.70	22.20
23	40	14.31	9.86	68.92	0.89	0.00	1.29	5.51	14.98	22.84	43.47
24	80	8.46	6.63	78.35	0.86	0.00	0.03	3.91	6.72	11.55	36.13
25	36	21.40	10.22	47.75	0.98	0.80	0.02	16.25	21.45	27.85	41.92
26	40	6.95	6.11	87.81	0.88	0.00	0.09	2.20	6.43	9.73	26.24
27	40	14.58	10.64	72.98	0.85	0.00	1.04	6.61	12.33	17.79	44.03
28	40	10.45	5.89	56.39	0.96	0.32	0.25	5.81	10.00	14.64	21.98
29	40	5.86	4.40	75.08	0.92	0.01	0.05	2.18	5.31	8.07	16.27
30	38	11.56	10.24	88.59	0.89	0.00	0.19	4.60	8.04	17.02	44.23
31	40	10.62	4.59	43.16	0.95	0.08	2.70	8.08	10.23	13.03	22.12
32	52	16.74	19.78	118.14	0.67	0.00	0.43	6.00	11.95	18.64	91.82
33	80	8.77	8.08	92.11	0.64	0.00	0.60	4.45	7.51	11.29	66.79
34	80	7.07	8.49	120.11	0.65	0.00	0.21	1.78	4.93	9.30	50.92
35	23	25.80	28.30	109.69	0.81	0.00	0.27	3.30	12.98	50.67	98.47
36	40	7.39	4.48	60.66	0.95	0.08	0.09	4.37	6.70	11.24	15.40
37	36	16.99	13.45	79.14	0.83	0.00	1.38	6.41	11.20	31.31	44.61
ALL	**35**	**11.31**	**5.86**	**51.80**	**0.89**	**0.00**	**3.99**	**7.02**	**8.77**	**14.59**	**25.80**

[1] N = number of data points submitted by the PAMS site. PAMS sites were requested to perform and report replicate determinations (i.e., 40 data points). Some PAMS sites performed multiple sets of replicate analyses on different instruments.
[2] MEANBIAS = arithmetic mean of bias values for all compounds reported by the particular PAMS sites.
[3] STD = sample standard deviation.
[4] CV = coefficient of variation = (STD/MEAN) x 100.
[5] NORMSTAT = normality statistic (from SAS, for sample sizes<2000). This is the Shapiro-Wilk "w" statistic which tests the null hypothesis that the data sample comes from a normal data distribution.
[6] PROBNORM = probability level for NORMSTAT (from SAS, for samples sizes <2000, probability of a smaller "w" statistic). For the data distribution to be considered NORMAL, the probability level must be 0.05 or larger for a 95% confidence level (accept the null hypothesis).
[7] MIN = minimum value from sample.
[8] Q1 = 25th percentile from sample.
[9] MEDIAN = 50th percentile from sample.
[10] Q3 = 75th percentile from sample.
[11] MAX = maximum value from sample.

Average Percent Bias per Organization

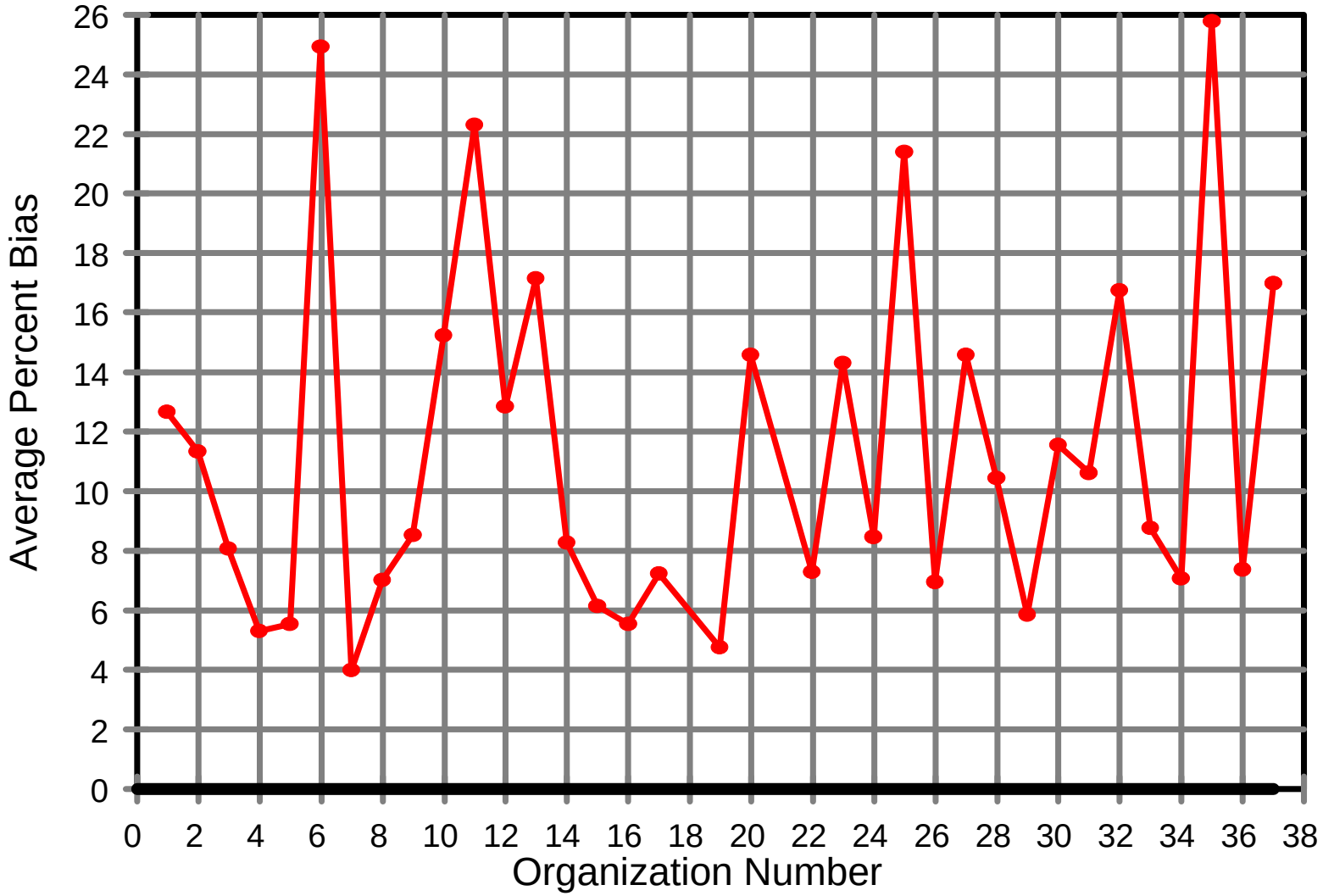

Figure 4-53. Average Percent Bias per PAMS Site for all Compounds

5.0 REFERENCES

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2. U. S. Environmental Protection Agency. Code of Federal Regulations. Draft Title 40, Part 58. *Enhanced Ozone Monitoring Regulations.* Washington, D. C. Office of the Federal Register. August 23, 1991.

3. U. S. Environmental Protection Agency. *Photochemical Assessment Monitoring Stations Implementation Manual: Network Design and Siting for PAMS.* Office of Air Quality Planning and Standards, Research Triangle Park, NC. EPA-454/B-93-051. March, 1994.

4. U. S. Environmental Protection Agency. *Technical Assistance Document for Sampling and Analysis of Ozone Precursors.* Office of Air Quality Planning and Standards, Research Triangle Park, NC. EPA-600/8-91-215. October 20, 1994.

Appendices

The appendices of this report contain the raw data which has been summarized in tables included in the body of the report. These appendices are very large and are not available in Adobe format.